EXHIBIT E

I, Warren James Woodford, PhD, declare as follows:

1. I reside in Chattanooga, Tennessee and am a Licensed Researcher with more than 30 years experience working in the field of odor science specializing in the detection of volatile organic chemicals (VOC, *i.e.*, odor molecules in air); in particular, the odors emitted by controlled substances. My training and experience involves odor testing using laboratory devices as well as human and canine olfaction (the science of "smelling") to detect and identify drug odors.

2. I developed and patented the Methyl Benzoate odor, which is in use as a dog training aid world-wide and is recognized as a scientific standard odor for the training, certification and proficiency testing of drug dogs to alert to the odor of cocaine. (See Exhibit 1, Mimicking the Aroma of Cocaine for Police Use, NEW YORK TIMES, April 11, 1981; Exhibit 2, United States Patent, Aroma of Cocaine, April 7, 1981.) Since 1981, when I received the patent for Methyl Benzoate, I have permitted Law Enforcement agencies and dog training facilities to use it freely.

3. I have testified in numerous jurisdictions about the training requirements and conditions for humans and canines to reliably smell-detect the odors emitted by controlled substances. My education, training, experience and publications are outlined in my *curriculum vitae*, which is attached as Exhibit 3. I have been retained as an expert, been deposed, and executed affidavits and declarations in numerous cases. A list of cases in which I have testified in the last four or more years is attached as Exhibit 4.

4. I reviewed the following documents supplied to me by Counsel in this case:

   a. Affidavit of Sanford Angelos;
   b. Affidavit of Dr. Lawrence Myers;
   c. Affidavit of David Kroyer;
   d. Claimants' Answer to Government's Motion for Summary Judgment;
   e. Affidavit of Officer Richard King 6/24/2010, including attachments (Photos, Various Logs, and Certification);
   f. Government's "Deny's False Alert Summary";
   g. Affidavit of Officer Richard King 12/21/2010;
   h. Preliminary Report of Dr. Lawrence Myers;
   i. Transcripts of Testimony from April 26-27, 2004 Motion to Suppress; and
   j. *United States v. Marrocco,* 730 F.3d 711 (7^{th} Cir. 2013).

5. I am in agreement with the Angelos, Myers, and Kroyer Affidavits regarding the technical training information, my patented invention, methyl benzoate, and with their descriptions of the nature of the odor as well as the quantitative amounts on currency, which they lay out in great detail. Affidavits attached as Exhibits 5-7, respectively. And I may testify as to the matters contained therein. I am the first person to discover and publish about the widespread contamination of cocaine on United States Currency in general circulation (1984 Atlanta news item; chronicled in the book *Bigger Secrets* (Houghton Mifflin, 1986); See also, Mark Curriden, *Courts Reject Drug-Tainted Evidence,* A.B.A. J. 22 (Aug. 1993), attached as Exhibit 8.

6. My testimony that 90% of U.S. Currency in general circulation contains cocaine is quoted in appellate court decisions, including, but not limited to, *United States v. U.S. Currency, $30,060.00*, 39 F.3d 1039, 1043 (9th Cir. 1994) (Recites testimony of Dr. James Woodford that ninety percent of all cash in the United States contains sufficient quantities of cocaine to alert a narcotics detection dog).

7. My testimony and expert opinion that ninety percent of the currency supply is tainted with drugs has been validated and confirmed by innumerable, peer-reviewed, scientific studies. *See e.g.*, Exhibit 9, David Biello, *Cocaine Contaminates Majority of U.S. Currency*, SCI. AM., Aug. 19, 2009.

8. I am of the opinion that methyl benzoate is a key element in the training of drug dogs to detect cocaine.

9. I am of the opinion that the so-called "Two hour theory" is not scientifically valid. The "two hour theory" purports to claim that a dog alert to currency provides a reason to argue (probable cause) that the currency was in close proximity to illegal drugs within two hours. The theory is flawed and has no basis in logic or science.

   a. In the two hour theory, it is theorized that the odor of cocaine (methyl benzoate) arises from the odor wafting through surrounding air from a bulk drug source through the open air so as to be absorbed by alleged currency in close proximity to the drug bulk. The theory derives from a Dr. Kenneth Furton and others using my patented material, methyl benzoate, to spike paper currency and then measuring the time it takes for the odor to evaporate.

   b. As I have commented, the Furton experiment is irreparably flawed because it does not consider real-world conditions. The experiment was done using "washed dollar bills;" *i.e.*, "cleansed currency"

ostensibly to perfect the two hour experiment by removing drug traces already present on the test currency. However, the washing procedure did not just remove the trace narcotics; it also removed the naturally occurring fingerprint oil (*i.e.*, "sebum") that literally coats real world, circulated currency. See Exhibit 10, Chemical, *Dog Experts Debunk Debunkers of "Contaminated Money Myth"*, CRIMINAL PRACTICE REPORT, Vol. 12, No. 23, November 18, 1998, at 460.

c. As I explained in The Criminal Practice Report (*id.*) soon after the Furton two hour theory was released, dollar bills (or currency) in general circulation contain sebum oil. The sebum holds cocaine molecules, as well as cocaine odor molecules (methyl benzoate), and encapsulates them similar to a "scratch and sniff" format.

d. Moreover, as described in my patent, changes in environmental conditions, *e.g.*, air temperature and humidity, surrounding the money, *i.e.*, the "headspace", can liberate methyl benzoate from ordinary (or "innocent") currency into the surrounding air at unpredictable times. In addition, officers can cause drug odor emission from money by jostling it during counting and/or handling prior to presenting the money to drug dogs.

e. In early scientific studies of my patent, methyl benzoate was referred to as an evaporating "adulterant" odor on normal currency in general circulation; again, it is not an "adulterant;" it is a naturally occurring odor generated by the crystals of cocaine embedded in the surface of currency and encapsulated in the sebum oil on the money. As Sanford Angelos explains in his affidavit, methyl benzoate is a by-product odor produced by cocaine. See Angelos Affidavit at ¶16.

f. Further, I am of the opinion that so-called "paper currency" in general circulation is not ordinary paper at all. Currency is actually produced from cotton and linen fabric. Crystalline cocaine (or cocaine powder) and cocaine base adhere to the fabric of the currency. Cocaine attached to surface of bills and encapsulated in the sebum oil contained on the currency will release (or off-gas) methyl benzoate at unpredictable times at the whims of temperature and humidity.

g. Early studies found that methyl benzoate *artificially applied* to the surface of "paper" evaporates below dog olfactory thresholds in ninety (90) minutes, or about an hour and a half, and it takes 2 hours for it all to evaporate from "paper". This "artificial currency",

and its flawed 90 minute time frame eventually became stretched to become the so-called "Within Two Hour Theory". However, as I explained *supra*, the washing of the currency transforms it by removing *both* any cocaine residues, and *critically*, the sebum oil. I am of the opinion that the sebum oil is a key component of generally circulated currency because it traps and holds cocaine as well as its odor – and releases trapped odor into the air by way of temperature and humidity changes, as well as handling the money.

h. I am of the opinion that the so-called Two Hour Theory is scientifically invalid for the reasons stated herein. Additionally, I know that the theory is flawed in practice because I have conducted *in-court* demonstrations using precisely measured relative amounts of methyl benzoate spiked onto "real world currency;" *i.e.*, *unwashed* and still containing sebum, that prove the odor of methyl benzoate lingers far longer than the theorized two hours. The odor persists on unwashed bills to the extent that humans can smell it for substantially longer periods of time than two hours. For example, I took part in a hearing in Oregon where the methyl benzoate odor lingered for at least two days at a level easily detectable by humans at the hearing. I am of the opinion that a canine's olfactory senses are far more sensitive than those of humans, therefore, I am of the opinion that if the humans could still smell the methyl benzoate, it is beyond question that any canine could do so. Indeed, a dog would be able to discern the odor for a far longer period of time than any human.

10. I am of the opinion that extinction training is essential in order to properly train a canine to detect so-called non-innocently contaminated currency. In the context of drug detection dogs, extinction training is the process by which a dog's nose is desensitized to the target odor, *i.e.*, to train dogs NOT TO ALERT to an amount of odor typically on currency in general circulation. In other words, it is a way to teach dogs "how much" odor level defines the odor signal for response.

a. Extinction training of dogs is necessary so that dogs do not alert and indicate to cocaine residue and by-product odor found on ordinary currency in general circulation. Rather, the dog is "extinction trained" to, and would only, alert to a relevant odor level of the methyl benzoate chemical and by-product odor of cocaine crystals sticking to surface of bills and stuck within the fibrous fabric of currency.

b. I am of the opinion that another problem inherent with using a dog

to sniff-test or search for currency is that the currency itself has an odor. Thus, another aspect of extinction training as it relates to currency is to minimize the dog's interest in the background odor of ink and any other residues (*e.g.* sebum) commonly found on **all** United States currency.

11. I am of the opinion that a problem that dogs have with paper currency is illustrated by experiments conducted on three Arkansas State Police dogs. *See* Exhibit 11, *Money Matters – Currency Contamination and the Law*, FORENSIC DRUG ABUSE ADVISOR, Vol. 7, No. 1, at 1 (1995). "In the first set of experiments, the dogs were exposed to four different samples of new uncontaminated, currency. All three dogs responded to three of the four clean paper samples as if they contained cocaine. Since it was obvious that the dogs were responding to uncontaminated currency, the researchers used unprinted plain bond paper, some of which had been contaminated with large amounts of cocaine (up to 5000 micrograms/bill). None of the dogs responded to plain bond controls, and they inconsistently responded to bond that had been contaminated." *See also,* J.M. Poupko, R.B. Holitik, J. Patnoe, *Studies on canine specificity and sensitivity for detection of cocaine on currency,* IN: PROCEEDINGS OF THE INT'L ASSOC. OF FORENSIC TOXICOLOGISTS/SOCIETY OF FORENSIC TOXICOLOGISTS JOINT CONGRESS, TAMPA, FL, 31 October – 4 November 1994 (Abstract 86).

12. I am of the opinion that it is necessary to conduct extinction training under "blind" scientific protocol so as to minimize trainers' and handlers' from potentially cueing a dog to alert. Without blind techniques testimony is routinely based on subjective "non-blind" episodes instead of verifiable, demonstrable episodes. One common result of reliance on non-blind testing conditions is an officer's testimony based on the "utilization records" or "field logs" containing post-deployment, field-use anecdotes written in the context of the trainer's and handler's personal beliefs.

13. I am of the opinion that extinction training is the proper way to teach dogs to reliably discriminate between the amounts of odor emitted from innocent bills which have cocaine stuck in the fibrous fabric that is releasing odor into the air and currency which has significantly higher amounts of emitted odors. *See e.g., Commonwealth v. Ramos*, 72 Mass. App. Ct. 773 (2008); *Washington's sniffer dogs re-trained to ignore pot and focus on hard drugs,* A.P., 31 May 2013, attached as Exhibit 12.

14. I am of the opinion that extinction training is scientifically valid because, without limitation:

a. It is not a novel technique;
b. It is generally accepted in the field of narcotic dog training;
c. It requires more qualifications and stringent standards of trainers and handlers than commonly found in self-certifying, non-extinction trained dog training programs;
d. It reveals the potential rate of error in applying dogs to currency;
e. It is part of the dog training literature on hand at training facilities;
f. It promotes minimization of subjective interpretations of dog trainers and handlers; and
g. It has gained court acceptance to the extent that it is deemed necessary.

15. I am of the opinion that dogs intended to be used for detection of narcotics, or specifically cocaine, should be dedicated currency dogs deployed solely for currency investigations. Additionally, I am of the opinion that dogs intended to be used for this purpose should be trained using methyl benzoate instead of so-called "street cocaine." My basis for this opinion was echoed in the Angelos and Kroyer affidavits. See paragraphs 6 and 9, respectively. Street cocaine contains unknown quantities of so-called cutting agents. Therefore, if one utilizes street cocaine to train a canine, one does not know what odors are actually present in the samples. Scientifically speaking, one would say that there is no control because the street cocaine contains unknown variables. By scientific definition, a dog trained with street drugs is not reliable because one could only speculate as to what odor the dog is detecting and consequently to which it is alerting.

16. In other words, by using methyl benzoate for extinction training, trainers and handlers can control the exact odor level per each dog's smell threshold to respond relevantly to currency. Since the level of odor in methyl benzoate dog training aids are exact known quantities of odor molecules, it allows for setting specific, objective conditions for when the dog should or should not alert and indicate to currency.

17. In context of this case, I agree with information in prior affidavits as accurate background research and add the following as it relates to the necessity of extinction training of dogs to teach them to discriminate between normal currency and from currency recently odor-tainted potentially due to being in close proximity with drugs. I am of the opinion that dogs that have not properly been trained using extinction techniques, methods, and procedures using methyl benzoate have no trained ability to discriminate between normal currency in general circulation and so called drug-related currency.

18. From my review of Canine documents in this case, the dog Deny apparently had not received any extinction training at the time of use in

this case.

19. I am of the opinion that extinction training to teach dogs to discriminate cocaine odor on currency is the same method and procedure for teaching dogs "discrimination" ability by way of "dead scent" extinction training used for "dead scents." A dead scent, also known as a residual odor, is an odor which is present in very small quantities because the source of the odor is no longer present. For example, assume that someone makes popcorn in a microwave and then leaves the room with the popcorn. Obviously, in this example, the popcorn is no longer in the room, but the odor of popcorn will remain for quite some time. Proper extinction training can teach dogs to ignore "dead scents." This is extremely important because:

a. Dogs' highly developed sense of smell causes them to alert and indicate to the stale remnants or traces of drugs already removed from the scene (or currency) under investigation.

b. The "dead scent" of methyl benzoate occurs on a majority (perhaps greater than 90%) of currency in general circulation.

c. Absent extinction training of dogs for currency discrimination there is no logical or scientific meaning for a positive dog alert and indication to questioned currency.

20. The facts in the record in this case demonstrate that Deny was not trained in this manner. For example, Officer King testified in his affidavit that Deny had previously alerted when no narcotics were found. *See* King Affidavit at ¶31. Assuming that Officer King was correct when he speculated that these positive alerts were due to narcotics previously being in proximity of the area to which Deny alerted, the only reasonable interpretation of King's admission is that Deny was alerting to a dead scent.

21. I am of the opinion that, absent methyl benzoate extinction training, there is not a logical or scientific basis that Deny's purported alert to the currency in question is probative of anything whatsoever. Or, in dog training language, there is no "proofing" to say that the dog Deny has any "discrimination" ability to separate "legitimate" currency from "drug related" currency.

22. I am of the opinion that in this case the only manner in which to verify the probative value of Deny's purported alert would have been to conduct a detailed crime laboratory analysis of the actual currency seized to precisely quantify the amount of methyl benzoate it was emitting. I saw

no evidence in the record that this was done; therefore, I am of the opinion that Deny's purported alert is not scientifically or logically meaningful.

23. I am of the opinion that at the time of the training (1998) and specific use of the dog Deny in this case, December 6, 2002, its trainers and handler knew or should have known that extinction training was key to base their opinions about use of the dog on currency in order for them to testify knowingly that Deny possessed by way of training the necessary "discrimination ability."

24. I am of the opinion that additionally, absent Deny's trainers and handler using commercially available methyl benzoate or conducting detailed laboratory testing to quantify the odor of their "street evidence" used for a training aid to determine exactly how much methyl benzoate was in the evidentiary material, there is no protection against conjectures by the handler for what the dog is being trained to do, *i.e.*, there is no basis for their "dog interpretation" court testimony.

25. I am of the opinion that in his affidavit, Sanford Angelos described factors that lead to the question of the reliability of Deny given the testing conditions, *i.e.*, "is it the currency or the room?" Angelos Affidavit at paragraphs 11-12. The Record reveals that the officers gave contradictory testimony about what they try to characterize as a "clean area" where Deny was deployed in this case. There are various reasons why the room itself could be a currency/narcotic odor source; there are skeletal details given of how they deployed Deny in the "clean area;" and there's no training literature for what the officers did. In my opinion, the squad room, baggage, lack of scientific controls within the deployment environment, testimony of prior use of the area for narcotics/currency investigations, contradictions in how the dog handler testified and an officer observing said another; and there is conflicting testimony about where the dog located the "secreted" currency. Even ignoring the critical lack of training, such imprecise testing conditions call into doubt any reliability in Deny's purported alert to the bag containing the currency.

26. In my opinion, because the dog had zero training to do what it was deployed to do (alleged discrimination of sniffing of currency), Deny could have been "led by the nose," *i.e.*, cued by the handler, to do what he did. The utter lack of any controls during Deny's purported sniff test means that the room exercise does not even rise to the level of junk science, let alone, scientifically reliable.

27. I am of the opinion that absent extinction training to currency it cannot be inferred, let alone proved, that Deny alerted and indicated to the

currency in this case in any reliable way to substantiate an argument that the currency in this case had recently been in contact with the airspace of illegal drugs. I agree with Dr. Lawrence J. Myers that there is no scientific evidence demonstrating that Deny's ability to detect cocaine translates into the ability to detect [the odor of] cocaine residue on money. And too, I agree with David Kroyer (certified drug dog training and behavior consultant) opinion that Deny was not trained to distinguish between the methyl benzoate odor and the odor of associated agents used for cutting cocaine, as well as the odor of ink on money. I emphasize that David Kroyer and Dr. Myers nailed the problem when they both offered that it is industry-standard to "proof-off" a drug dog to uncontaminated currency, *i.e.*, to ensure and validate that the drug dog does not alert to uncontaminated money, which is the goal of extinction training. The evidence from the handler in this case indicates that Deny was not "proofed-off" of uncontaminated currency.

By: Warren James Woodford

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EXHIBIT 1

The New York Times

SATURDAY, APRIL 11, 1981

Mimicking the Aroma Of Cocaine for Police Use

Law enforcement officers may want to familiarize themselves with the distinctive odors of narcotics. Patent 4,260,517, granted this week to Warren J. Woodford of Atlanta, offers a way to reproduce the aroma of cocaine, using readily available and noncontrolled substances.

Methyl benzoate is described as the substance responsible for the aroma of pure cocaine. A mixture provides the aroma of "street cocaine," covering the variety of different grades or purity that are sometimes affected by geographic origin, using methyl cinnamate and the dimethyl ester of truxillic acid. The compounds, in capsules, are released when it is desired to provide the aroma.

It is reported that efforts to reproduce the aroma of marijuana have recently been successful; previous attempts with cocaine had failed.

EXHIBIT 2

United States Patent [19]
Woodford
[11] **4,260,517**
[45] **Apr. 7, 1981**

[54] **AVAILABLE AROMA OF COCAINE**

[76] Inventor: **Warren J. Woodford**, 585 Lakeshore Dr. NE., Atlanta, Ga. 30307

[21] Appl. No.: **914,351**
[22] Filed: **Jun. 12, 1978**
[51] **Int. Cl.**[3] **C09K 3/00**
[52] **U.S. Cl.** .... **252/408**; 252/522 R; 252/522 A; 424/2; 427/2
[58] **Field of Search** 252/522, 408, 316; 427/2; 424/2

[56] **References Cited**

PUBLICATIONS

CA 88; 32647z, Forensic Chemistry p. 2, 1978.
U.S. Pharmacop's XVIII, p. 137.
Amalytical Manual, Gunn—10/2/74.
Washington Star 12/4/77.

Primary Examiner—Sam Silverberg
Attorney, Agent, or Firm—Jones, Thomas & Askew

[57] **ABSTRACT**

A method and product for providing the aroma of cocaine to the olfactory senses by volatilizing methyl benzoate and diluting said volatilized methyl benzoate with a non-odor masking gaseous diluent, such as air, and by then contacting the olfactory senses with the diluted mixture of volatilized methyl benzoate and gaseous diluent, whereby the aroma of cocaine is perceived. The aroma of "street cocaine" may similarly be provided by volatilizing and diluting a mixture of methyl benzoate, methyl cinnamate and the dimethyl ester of truxillic acid.

12 Claims, No Drawings

EXHIBIT 3

CURRICULUM VITAE

WARREN JAMES WOODFORD, Ph.D., Chemist
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EDUCATION

B.S., Chemistry, East Carolina University, 1968.
M.S. & Ph.D., Chemistry, Emory University, 1973.
Postdoctoral, Medicinal Chemistry, Kansas University, 1974.

PUBLISHED BIOGRAPHICAL INFORMATION

Who's Who in Frontiers of Science and Technology.
American Men and Women in Science.

MEMBERSHIPS

American Chemical Society.
American Association for the Advancement of Science.

LICENSE & CERTIFICATES

Researcher License, State of Tennessee Department of Health (License No. 10410) for activities regarding Scientific Research, Chemical Analysis of Controlled Substances, and Training of Odor Detection Animals.

Controlled Substances Registration Certificates, United States Department of Justice, August 1989 through May 1997, for Analytical Lab Activities regarding testing of controlled substances in Schedules 1, 2, 3, 3N, 4, 5. From June 1997 to present, am permitted to conduct independent examinations and testing of controlled substances on a case-by-case basis in licensed crime laboratories.

Drug Recognition and Evaluation Overview Course on NHTSA Manual, Certificate of Completion, Atlanta, Georgia, May 20-22, 2004.

Medical Review Officer (MRO) Federal Health & Human Services Training Course, Certificate of Completion, Chicago, Illinois, November 1-3, 1996.

FORENSIC WORK

Examined and tested a large variety of controlled substances at New Scotland Yard's Forensic Sciences Laboratories in London, England; as a visiting scientist, focused on forensic laboratory testing methods, October 1975.

For 38+ years have conducted numerous examinations of evidence and testing for controlled substances at various American crime laboratories and police station evidence rooms.

Researched marijuana cultivation, laboratory testing, and smell identification in the Bibliographic Area of the Institute of Pharmaceutical Sciences (United States government marijuana farm), in Oxford, Mississippi, May 1980.

Conducted laboratory studies regarding the GC/MS testing method for marijuana at the United States Army Forensic Drug Testing Laboratory, Wiesbaden, West Germany, July 1986.

Observed odor-detection K-9s in action with their police handlers in Croatia, Hungary & Poland, July 1999.

For about 15 years studied and worked with Thomas A. Knott, retired Baltimore police K-9 trainer and handler who was also a K-9 trainer/handler consultant for the FBI, HRT (Hostage Rescue Team), and the White House K-9 Corps. Observed his use of K-9s and his demonstrations with K-9s many times. He gave me access to his vast library on the subject of K-9 training and handling. Collaborated with other police K-9 trainers and advised handlers regarding K-9 training for smell-detection of controlled substances. Associative membership in the National Narcotic Detector Dog Association, 2007-2011.

Participant variable surface tracking (VST) K-9 certification sessions, American Kennel Club, Athens, GA, October 1994.

EXPERT TESTIMONY

Qualified as an expert witness on the subject of laboratory testing of controlled substances and testified more than 500 times (1975 to present) in many State Courts, Federal Courts, and Military Courts in the continental United States and abroad.

Qualified as an expert witness on the subject of training requirements and conditions for humans to reliably smell-detect odors of controlled-substances and testified in Federal Courts in Florida, Oregon, Washington, California, and Texas; and in State Courts in Georgia, New Mexico, Ohio, Indiana, Colorado, Washington, and Vermont.

Qualified as an expert witness on the subject of training requirements and conditions for K-9s to reliably detect odors of controlled substances in Federal Courts in California and in Washington, D.C. (testimony also incorporated into various other Federal jurisdictions such as Tennessee) and have testified on this subject in State Courts in Pennsylvania, Oregon, Nebraska, and South Dakota.

AUTHORED WORK

***Expert Evidence in Criminal Law: The Scientific Approach*, Published by Irwin Law, Inc., Pages 120-121, 2009. Subject: Mathematical analysis of Police observations of drug detection.**

***Endogenous Alcohol in Blood Can Add to BAC Levels, Proceedings of the 51st Annual Meeting of the American Academy of Forensic Sciences, Abstract No. E-10, page 133, 1999.* Subject: dietary alcohol volatilizes upon heat incubation prior to headspace gas chromatograph testing of blood.**

***Crime Lab Shortcuts Make for Bad Chemistry in Court*, Bureau of National Affairs, *Criminal Practice Manual*, Volume 9 (12), page 281, 1995. Subject: Interview regarding common errors made by crime laboratories during the testing of controlled substances.**

***Guidelines for DRE (Drug Recognition Evaluation)* (co-author), American Academy of Forensic Sciences, 40th Annual Meeting, San Antonio, Abstract No. E-15, page 124, 1994.**

Affidavit, Drug Testing Legal Manual, **Clark Boardman Co., page B8-1, 1989. Subject: laboratory testing errors in urinalyses of controlled substances.**

Detection of the Parkinsonism-Producing Neurotoxin, MPTP, **Academic Press, New York, page 543, 1986. Subject: co-developed assay method for neurotoxic impurity in controlled substances with scientists at the Centers for Disease Control (CDC) in Atlanta, Georgia.**

The Relation Between Paraquat Spills and Brain Damage, DEA Final Environmental Impact Statement, **Ace-Federal Reporters, Washington, D.C., page 282, 1986.**

Assay for Neurotoxin, Symposium on MPTP, **Department of Neurology, Uniformed University of the Health Sciences, Bethesda, Maryland, page 61, 1985. Subject: method for detecting neurotoxic impurity in controlled substances; co-developed with scientists at the Centers for Disease Control (CDC) in Atlanta, Georgia.**

How to Interpret Breath Alcohol Reports, **Library of Congress 83-51151, 1983.**

Synthesis of 5-substituted 2'-deoxyuridines, Journal of Medicinal Chemistry, **(co-author) Volume 19, page 909, 1976. Subject: Cancer therapeutic drug.**

Screening Procedures for Drugs, Journal of Chromatography, **Volume 115 (2), page 678, 1975. Subject: demonstration of errors in a crime laboratory method of testing controlled substances.**

Synthesis of the Alpha and Beta Anomers of 1- (2-deoxy-D-ribofuranosyl)-4'-pyridone, Journal of Medicinal Chemistry, **(co-author), Volume 17, page 1027, 1974. Subject: Cancer therapeutic drug.**

Synthesis and Cyclization. An Approach to pseudo-santonin; Dissertation Abstracts International, **Volume 34 (2), page 603, 1973. Subject: The odor ingredient in Absinthe,**

The Gas-phase Synthesis and Reactions of Bromamine, Inorganic Chemistry, **(co-author) Volume 8 (4), page 998, 1969. Subject: Bromamine in human breath is a biological marker for asthma, bronchitis and emphysema (i.e., chronic obstructive pulmonary disease, COPD).**

ACKNOWLEDGMENTS

What the Nose Knows; the Science of Scent in Everyday Life, **Crown Publishers, NY, pages 31-33, 71-72, 2008. Subject: odor identifications of marijuana and cocaine.**

Criminal Practice Report, Who Really Knows What a Dog's Nose Knows? **Pike & Fischer, Inc. (subsidiary of The Bureau of National Affairs) Volume 12, No. 23, page 462, 1998. Subject: methyl benzoate; the actual odor of cocaine.**

Indoor Air Pollution and Health, **Marcel Dekker, Inc., Chapter 15, page 337, 1996. Subject: Biological markers for volatile organic compound (VOC) odors from indoor air exposures. Co-contributor with scientists from the Oregon Health Sciences University in Portland, Oregon and the Centers for Disease Control (CDC) in Atlanta, Georgia.**

American Bar Association Journal, **August issue, page 22, 1993. Subject: cocaine traces on currency produce methyl benzoate, the odor of cocaine.**

Scientific Evidence **(Cumulative Supplement), The Michie Company, page 128, 1989. Subject: By testing a woman using the male scale, she will inevitably score as though she had consumed more alcohol than in fact she has.**

Electronic Supervisor **(United States Congress Office of Technology Assessment), Document OTA-CIT-333, pages 133-4, 1987. Subject: origin of false-positive test results on urinary metabolites of a marijuana.**

Journal of Immunological Methods, **Volume 101, page 50, 1987. Subject: contribution to the U.S. Public Health study by the Centers for Disease Control (CDC) regarding improving laboratory equipment for drug testing based on immunoassays.**

Substance Abuse Report, **April issue, page 7, 1986. Subject: marijuana metabolite testing flawed by a melanin by-product.**

Bigger Secrets**, Houghton Mifflin Co., Boston, Chapter 10, page 77, 1986. Subject: detection of cocaine residues on United States Currency in general circulation.**

Designer Drugs**, CompCare Publications, Minneapolis, Chapter 5, page 111, 1986. Subject: "Woodford/Vogt Test"; a detection method for a neurotoxin by-product in "designer drugs"; co-developed with Dr. Robert Vogt, laboratory scientists at the Centers for Disease Control (CDC) in Atlanta, Georgia.**

The Champion**, Volume IX (4), page 4, 1985. Subject: Equipment and testing method for determining human lung breath-to-blood ratios.**

Substance Abuse: Pharmacologic and Clinical Perspectives**, John Wiley and Sons, New York, page 63, 1983. Subject: chemical definition of "Cocaine Freebase".**

Analytical Chemistry Reviews**, Volume 51 (5), page 258R, 1979. Subject:** ***Screening Procedures for Drugs, Journal of Chromatography*****, Volume 115 (2), page 678, 1975. Subject: Evaluation of crime laboratory testing methodology for drug testing.**

RESEARCH GRANTS

United States Public Health Service (Department of Health & Human Services) CA54401 and CA55401.

PATENTS

United States Patent No. 4,260,517, My patented formulation of methyl benzoate, the odor of cocaine, was tested and found effective for human and canine smell-training and proficiency testing; available to K-9 trainers and handlers from Sigma Chemical Co., Forensic Chemistry Catalog No. P2423-100G. ***Mimicking the Odor of Cocaine for Police Use, New York Times*****, April 11, 1981. Confirmed as the actual odor of cocaine that canines** ***alert*** **and** ***indicate*** **to (Odor confirmed by other scientists:** ***Proceedings of the 51st Annual Meeting of the American Academy of Forensic Sciences, Abstract No. B-28, page 33, 1999).***

United States Patent No. 4,843,020, Improved GC/MS method and solutions to eliminate false-positive test results for marijuana.

October 2014

EXHIBIT 4

I testified as an expert witness in the following cases during the past eight years to date:

2010

State of Georgia v. Guintivano, Clarke County State Court, Attorney Ben Sessions, Judge Simpson, Jury Trial. Subject Infrared Breath Alcohol Testing.

State of Georgia v. Newman, Columbia County Superior Court, Attorney Victor Hawk, Judge Brown, Re-trial by Jury. Subject: Assay Blood Alcohol Gas Chromatography Testing.

State of Georgia v. King, Douglas County State Court, Attorney Trina Griffiths, Judge Dettmering, Jury Trial. Subject: Alcohol Infrared Breath Testing.

State of Georgia v. Sinon, Houston County State Court, Attorney Robert Daniel, Judge Richardson, Jury Trial. Subject: Alcohol Infrared Breath Testing.

State of Georgia v, Schiavone, Hall County State Court, Attorney Watson, Judge Baldwin, Jury Trial. Subject: Alcohol Infrared Breath Testing.

State of Vermont v. Bryant, Lamoille District Court, Attorney Paul Volk, Judge Pearson, Motions Hearing. Subject: Human olfactory observations.

City of Macon Georgia v. Britt, Attorney Debra Gomez, Judge Herndon, Administrative Hearing. Subject: Assay Drug GCMS Testing False Positives.

State of Georgia v. Tylor, Jones County Superior Court, Attorney Mary Stanley, Judge George, Jury Trial Subject: Alcohol Infrared Breath Testing.

Connecticut Board Department of Public Health v. LaChance, Attorney Kardaras, Hearing Officer Gaither, Administrative Hearing. Subject: Drug GCMS Testing.

Smith County Tennessee Education Association v. Smith County Board of Education, United States District Court of the Middle District of Tennessee at Nashville, Attorney Rick Colbert, Judge Campbell, Deposition. Subject: Teacher Drug Testing.

State of Georgia v. Ibarra, Coweta County State Court, Attorney Allen Trapp, Judge Cranford, Jury Trial. Subject: Alcohol Infrared Breath Testing.

Department of Labor and Industries, Industrial Insurance Division, State of Washington, In re: Lolkus, Attorney Hunter Macdonald, Deposition. Subject: Volatile Organic Chemicals (VOC); indoor-air work environment.

State of New Jersey v. Macaluso and Rivers, Bergen County State Court, Judge Roma, Attorneys James Bustamante and David Michael. Subject: Human and canine olfactory observations.

State of California v. Paralta, City & County Superior Court of San Francisco, Attorney Marshall Schulman, Judge Chan. Subject: Human olfactory observations.

Smith County Tennessee Education Association v. Smith County Board of Education, United States District Court of the Middle District of Tennessee at Nashville, Attorney Rick Colbert, Judge Campbell. Bench Trial. Subject: Teacher Drug Testing.

2011

State of Florida v. Sanchez, Collier County Circuit Court, Judge Hardt, Attorney David Macey, Evidentiary Hearing. Subject: Human olfactory observations.

State of Georgia v. Mobley, Bibb County State Court, Attorney Bob Daniel, Macon, Georgia, Judge Adams, Bench Trial. Subject: Alcohol Infrared Breath Testing.

State of Georgia v. Lafferty, Bibb County State Court, Attorney; Bob Daniel, Macon, Georgia, Judge Adams, Jury Trial. Subject: Alcohol Infrared Breath Testing.

State of Georgia v. Burton, Houston County State Court, Attorney Bob Daniel, Macon, Georgia, Judge Ashford, Jury Trial. Subject: Alcohol Infrared Breath Testing.

State of Georgia v. Seymour, Athens-Clarke County State Court, Attorney Doug Lenhardt, Athens,, Georgia, Judge Simpson, Jury Trial. Subject: Alcohol Infrared Breath Testing.

State of Georgia v. Yarrington, Cobb County State Court, Attorney Steven Ward, Atlanta, Georgia, Judge Glover, Jury Trial. Subject: Alcohol Infrared Breath Testing.

People of Illinois v. Maloney, Henry County Circuit Court, Attorney Steve Hanna, Moline, Illinois, Judge Hammer, Evidentiary Hearing. Subject: Human Olfactory Observations.

State of Georgia v. Ford, Athens-Clarke County Georgia State Court, Attorney Steven Ward, Atlanta, GA, Judge Simpson, Jury Trial: Subject: Alcohol Infrared Breath Testing.

State of Nebraska v. Doyle, Lancaster County District Court, Attorney Sara Zalkin, San Francisco, and John Berry, Lincoln, Nebraska, Judge Flowers. Evidentiary Hearing. Subject: Canine Olfactory Observations.

State of South Dakota v. Delgado, Pennington County Circuit Court, Attorneys J. Tony Serra, San Francisco, CA, and Timothy J. Rensch, Rapid City, S.D., Judge Thorstenson. Evidentiary Hearing. Subject: Canine Olfactory Observations.

People of California v. Cole, Sonoma County Superior Court, Attorneys Erica E. Treeby and J. Tony Serra, San Francisco, CA, Judge Medvigy, Evidentiary Hearing. Subject: Canine Olfactory Observations.

2012

State of Georgia v. Rodriguez-Zepeda, Hall County Georgia Superior Court, Attorney Jim Hodes, Atlanta, GA, Judge Gosselin, Bench Trial. Subject: Net Weight of Evidence.

State of Georgia v. Putmon, Fulton County Georgia Superior Court, Attorney Michael Holmes, Atlanta, GA, Judge Schwall, Evidentiary Hearing. Subject: Human Olfactory Observations.

State of Georgia v. Ford, Athens-Clarke County Georgia State Court, Attorney Steven Ward, Atlanta, GA, Judge Simpson, Jury Re-Trial: Subject: Breath Alcohol Testing.

State of Georgia v. Patanode, Hall County Georgia State Court, Attorneys David Powell and Jeffery Talley, Gainesville, GA, Judge Wynne, Jury Trial. Subject: Prescription Drug Testing.

State of Georgia v. Ladow, Fulton County Georgia Sate Court, Attorney Lawrence Kohn, Atlanta, GA, Judge John R. Mather, Jury Trial. Subject: Breath Alcohol Testing.

State of Georgia v. Jenkins, Fulton County Georgia State Court, Attorney Charles T. Magarahan, Atlanta, Judge Fred C. Eady, Jury Trail. Subject: Breath Alcohol Testing.

State of Georgia v. Bonnick, Gwinnett County Georgia State Court, Attorney Russell Burnett, Atlanta, Judge Randy Rich, Jury Trial. Subject: Breath Alcohol Testing.

State of Georgia v. Miller, Bartow County Georgia Superior Court, Attorneys Steven Ward (Atlanta) and Trina Griffiths (Marietta). Judge David Smith. Jury Trial. Subject: Breath Alcohol Testing.

State of Washington v. Fager, Jefferson County Superior Court, Attorneys Michael Haas (Port Townsend) and James Dixon (Seattle). Judge Craddock Verser. Evidentiary Hearing. Subject: Human Olfaction.

State of North Carolina v. Stough, Jackson County Criminal Superior Court, Attorneys Roy Patton (Sylva) and Ben Scales (Ashville). Judge Allen Thornburg. Jury Trial. Subject: Methamphetamine Testing.

2013

State of California v. Phillips, *et al*., Orange County Superior Court, San Francisco Attorneys: Tony Serra, Shari White, Kali Grech, and Gregory Bentley, Judge John D. Conley. Evidentiary Hearing. Subject: Human Olfaction.

State of Georgia v. Cho, Gwinnett County State Court, Attorney Kevin Mooney (Atlanta), Jury Trial. Subject: Breath Alcohol Testing.

State of Georgia v. Karimi, Forsyth County State Court, Attorney Charles Magarahan (Atlanta), Chief Judge T. Russell McClelland, III, Jury Trial. Subject: Breath Alcohol Testing.

State of Georgia v. Kinney, Fulton County State Court, Attorney James K. "Skip" Sullivan (Atlanta), Judge Diane E. Bessen, Jury Trial. Subject: Breath Alcohol Testing.

Rothenberg, *et. al*., v. The New York City Taxi and Limousine Commission, and The City of New York, *et. al*., United States District Court Southern District of New York, Attorneys Dan Ackman and Norman Siegel (New York), Deposition. Subject: Workplace Drug Testing.

State of Ohio v. Aliu, *et. al.*, Lorain County Court of Common Pleas, Attorneys Michael Duff, Dan Whiteman (Cleveland, OH), and Eber Bayona (Norwalk, CA), Judge James M. Burge. Evidentiary Hearing. Subject: Human and K-9 Olfaction.

State of Washington v. Espinoza, et al, Pierce County Superior Court, Attorney Lisa Mulligan (Seattle), Ephraim Benjamin (Tacoma), Michael Negle (Olympia), Judge Ronald E. Culpepper. Evidentiary Hearing. Subject: Canine Olfaction.

American Federation of Government Employees (AFGE) Local 2585 and the Federal Mediation and Conciliation Services, DOJ Bureau of Prisons, FCI Bennettsville, South Carolina, Re: Slover, Attorney Evan Greenstein, Arbitrator: Harry Mason Arbitration Hearing. Subject: Prison Drug Testing.

United States of America v. Wiggins, District Court for the District of New Mexico, Federal Defender Attorney Marc Robert, Judge William Johnson, Evidentiary Hearing, Subject: Probation Drug Testing.

State of Georgia v. Brischler, State Court of Dekalb County, Georgia, Attorney Charles T. Magarahan, (Atlanta), Judge Johnny N. Panos, Jury Trial. Subject: Breath Alcohol Testing.

2014

State of Georgia v. Amick, State Court of Hall County, Georgia, Attorney Gus McDonald, Cornelia, Georgia, Judge Larry A. Baldwin, II, Jury Trial. Subject: Blood Alcohol Testing.

Sate of Georgia v. Wandel, Coweta County State Court. Attorney John Travis Overocker, Carrolton, GA, Judge John Herbert Cranford, Jury Trial. Subject: Breath Alcohol Testing.

State of Indiana v. Conkright, Vanderburg County Superior Court, Attorneys Glenn Grampp and Patrick Duff, Evansville, IN, Judge Wayne Trockman, Evidentiary Hearing. Subject: Human olfactory observations.

State of Georgia v. Slabbaert, Fulton County State Court, Attorney Steven Ward, Atlanta; Judge Myra H. Dixon, Jury Trial. Subject: Breath Alcohol Testing.

State of Texas v. Jones, Montgomery County, 359th District Court, Attorneys Luro Taylor, Houston, and Patty Miginnis, Conroe; Judge Kathleen Hamilton. Evidentiary Hearing. Subject: K-9 olfactory observations.

State of Georgia v. Long, Fulton County State Court, Attorney Charles T. Magarahan, Atlanta, Judge Fred C. Eady, Jury Trial. Subject: Breath Alcohol Testing.

State of Georgia v. Woody, Superior Court of Dawson County, Charles T. Magarahan, Atlanta, Judge Jason Deal, Jury Trial. Subject: Breath Alcohol Testing.

State of Georgia v. Kim, Gwinnett County State Court, Attorney Kevin Mooney, Atlanta, Judge Emily Brantley, Jury Trial. Subject: Breath Alcohol Testing.

October 2014

EXHIBIT 5

IN THE
UNITED STATES DISTRICT COURT
OF THE NORTHERN DISTRICT OF ILLINOIS
EASTERN DIVISION

UNITED STATES OF AMERICA Plaintiff, vs. FUNDS IN THE AMOUNT OF ONE, HUNDRED THOUSAND AND ONE HUNDRED TWENTY DOLLARS ($100,120.00 U.S.C.), Defendant.	)	No. 03 C 3644 Honorable Elaine E. Bucklo, District Judge, Presiding.
NICHOLAS P. MARROCCO, and VINCENT J. FALLON, Claimants.	)	

State of Illinois)
) SS.
County of Cook)

AFFIDAVIT

I, SANFORD A. ANGELOS, first being duly deposed and sworn, state the following:

1. That your affiant is of legal age, sound mind and under no legal disability.

2. That your affiant is a Forensic Chemistry Consultant in private practice as Aris Associates Ltd. As such, my primary employment is as a contract Forensic Specialist Instructor for the United States Government. I have worked for the Department of Justice, International Criminal Investigation Training Assistance Program (ICITAP). I have also worked with the Department of State, the Bureau of International Narcotics and Law Enforcement Affairs (INL), in the same capacity. I retired as an employee of the United States Department of Justice, Drug Enforcement Administration (DEA) on

January 20, 2006 after 30 years of government service. Up to that time I was employed in the capacity of Senior Forensic Chemist. My statements in the sections below are based on my knowledge, skill, experience, training and education. My experience, education and training are described in detail in Exhibit A.

3. That your affiant, if called to testify, would state that Exhibit A is my *curriculum vitae*. I would testify that the statements made therein are true and correct. Further, I have been found to be an expert witness in United States District Courts and in the various courts of the States of the United States as a Forensic Chemist with over 30 years of experience. I have been permitted to offer my opinions to a reasonable degree of scientific certainty in cases where I have been called on behalf of the United States and sometimes on behalf of private litigants.

4. That I have completed the review of the United States' Renewed Motion for Summary Judgment and the Rule 56.1(a)(3) Statement of Material Facts as well as transcripts of testimony in a Motion to Suppress, that were provided. I also reviewed several other documents that consisted of various scientific articles, manuals, reports, court filings and letters. A list of the items with brief comments is attached as part of this report.

5. That the opinions expressed in this affidavit are based on my more than 30 years of experience as a forensic chemist in the employ of the United States government together with my practical experience in the laboratory on behalf of my employer. Each of the opinions expressed are to a reasonable degree of scientific certainty.

6. That Cocaine (benzoylmethylecgonine) is a stable crystalline tropane alkaloid

obtained from the leaves of the coca plant. Cocaine in its purest form is a white, pearly product. Cocaine appearing in powder form is a salt, typically cocaine hydrochloride. Street market cocaine, or illicit cocaine, is frequently adulterated or "cut" with various powdery fillers to increase its weight. Cocaine is readily available in all major countries' metropolitan areas. Since 1985 there have been several scientific studies investigating the issue of cocaine contamination on currency. The studies *infra*, are of the type of studies relied upon by professional forensic chemists:

A. In a 1985 study done by the U.S. Drug Enforcement Administration forensic laboratory in Chicago, Illinois, on the money from a U.S. Federal Reserve district bank, random samples of shredded $50 and $100 banknotes revealed that a third to half of all currency tested bore traces of cocaine. Moreover, the machines themselves were often found to test positive, meaning that subsequent batches of cash fed through them would also become contaminated with cocaine residue.[1]

B. In a 1989 study conducted by the Royal Canadian Mounted Police Forensic Laboratory in Regina, Saskatchewan, the Forensic Lab determined that currency provided by the Bank of Canada was contaminated. In the Canadian study, 100 banknotes of each denomination were analyzed. All of the money had cocaine at a level less than 10 nanograms* per note.[2]

   *Please note: 1 gram equals 1000 milligrams; 1 milligram = 1000 micrograms; 1 microgram = 1000 nanograms

C. In 1996, a study from the National Institute on Drug Abuse, Baltimore, Maryland, was published. It examined $1 denominations collected from 14 cities in the United States. Cocaine was found on 79% of the currency samples in amounts above 0.1 micrograms (or 100 nanograms). Currency samples with amounts above 1.0 micrograms (or 1000 nanograms) were found in 54% of the samples. The highest amount detected on a single banknote was determined to be 1327 micrograms, or 1.327 milligrams. The study also

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[1] Angelos, S.A., Unpublished Report "Trace Analysis of U.S. Currency"U.S. Drug Enforcement Administration, Forensic Science Section, (1985).
[2] Hudson, J.C., Analysis of Currency for Cocaine Contamination, *Can. Soc. Forens. Sci. J.*, **22**:2:203-218 (1989).

determined that the paper matrix of US currency has the ability to bind with cocaine.[3]

D. In 1998, another study was conducted in Chicago, Illinois. This study found that 100% of ten $20 banknotes randomly collected in Rockford, Illinois were contaminated with cocaine. These bills had cocaine amounts from a low of 0.14 micrograms to a high of 10.02 micrograms. This study also tested four $1 banknotes from Chicago and four uncirculated $1 banknotes from the U.S. Federal Reserve district bank to be used as a control sample. All four of the uncirculated $1 bills of the control sample were found not to have cocaine. While three of the four circulated $1 banknotes did have cocaine contamination. As a result of the single clean $1 banknote, the study reports 92.8% of the currency analyzed had cocaine contamination.[4]

E. A study reported in 2001, by the Cuyahoga County Coroner, Cleveland, Ohio, showed results of 92% of the bills analyzed positive for cocaine. The study had randomly selected ten $1 banknotes from five cities, a total of 50 bills. One city was Chicago, Illinois and another was San Juan, Puerto Rico; the analysis was conducted at National Institute on Drug Abuse. This study determined that the lowest contamination of cocaine was 0.01 micrograms (or 10 nanograms), while the highest amount was 922.72 micrograms (or 922,720 nanograms). The study is significant in that it also looked for other drugs. It reports that heroin, amphetamine, methamphetamine and PCP were also detected on the banknotes.[5]

F. The next study was in 2008. All denominations of currency were collected from three Massachusetts cities with a total of 31 banknotes. A control sample was obtained from a local bank. Cocaine was detected on 67% of the banknotes. All ten of the uncirculated banknotes were negative. The lowest amount of cocaine was reported to be about 2 nanograms, while the highest amount was 49.4 micrograms per banknote.[6]

G. The same researcher expanded the study in 2009 and reported that 90% of 234

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[3] Oyler, J., Darwin, W.D., and Cone, E.J., Cocaine Contamination of United States Paper Currency, *J. Analytical Toxicology,* **20**:4: 213-216 (1996).
[4] Negrusz, A., Perry, J.L., and Moore C.M., Detection of Cocaine on various Denominations of United States Currency, *J. Forens. Sci.,* **43**:3 (1998).
[5] Jenkins, A.J., Drug Contaminations of US Paper Currency, *Forens. Sci. Intnl.,***121** (2001).
[6] Zuo, Y., Zhang, K., Wu, J., Rego, C., and Fitz, J., An Accurate and Nondestructive GC method for determination of Cocaine on US Paper Currency, *J. Separation Sci.,* **31** (2008).

United States' banknotes of varying denominations tested positive and were contaminated with cocaine. The amounts were reported as low as 0.006 micrograms (or 6 nanograms) to high as over 1240 micrograms (or 1,240,000 nanograms). The banknotes were collected from seventeen different cities. This study also included many other countries.[7]

7. That based on review of these studies, I hold the opinion, to a reasonable degree of scientific certainty, the studies indicate United States Currency in general circulation is contaminated with illicit drugs and most often with cocaine. Further, the widespread contamination of currency has been increasing from 33% in 1985, to 79% in 1996, to over 90% in 2001. It has been repeatedly shown that there is a range of contamination in all of the studies; the range is due to cross contamination. When a cocaine-contaminated banknote is processed through a sorting or counting machine, traces of the drug are easily passed to other bills in the same batch. Automated Teller Machines (ATMs) serve to spread tiny amounts of cocaine to nearly all the currency they distribute, as do the counting machines used in banks and casinos. It is of particular interest that the study in 1996, determined the highest amount on a banknote to be **1327 micrograms**, and the 2009 study found a high of over **1240 micrograms**. Therefore, the level of major contaminations has basically remained constant. Science cannot determine what amount is due to primary contamination, such as during a drug deal or use, and how much is due to secondary contamination, such as during interaction between contaminated and uncontaminated banknotes. It only takes one bill to contaminate

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[7] Zuo, Y., *et.al.*, Unpublished presentation to the American Chemical Society.

hundreds, or even thousands of others; thus, the number of banknotes that have actually come into direct contact with the drug trade is far smaller.

8. That although cocaine is very stable with a melting point of 198° C, it will breakdown into several different compounds when exposed to moisture. Many of these components are of forensic value. However, a minor breakdown compound is of the most concern in this case. Methyl benzoate is a fragrant liquid with a boiling point of 199° C, however, it is considered combustible with a flash point of 83° C. One study examined the breakdown of cocaine hydrochloride when in storage as evidence. It showed that cocaine is stable but will 'off-gas', or release, a vapor of methyl benzoate. The amount of vapor was determined to be 1.89 nanograms per minute at room temperature and dry conditions, 2% relative humidity; to a high of 62 nanograms per minute at 40° C and 80% relative humidity. An increase of temperature to 40° C and a 2% relative humidity would produce 29 nanograms of methyl benzoate per minute. The study determined that even at high temperatures and high humidity only 1.48% of the cocaine hydrochloride was depleted.[8]

9. That it has been shown drug detector canines are keying on both the vapor of illicit cocaine and the fragrant methyl benzoate. In 1996, a study that trained canines to alert to methyl benzoate and then tested their response to cocaine hydrochloride discovered that methyl benzoate is not the detection odor signature for cocaine.[9]

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[8] Dejarme, L.E., Gooding, R.E., Lawhon, S.J., Ray, P., and Kuhlman, M.R., Formation of Methyl Benzoate from Cocaine hydrochloride under Different Temperatures and Humidies, *Proceedings. SPIE*, **2937:**19 (1996).

[9] Waggoner,L.P., Jonston, J.M., Williams, M., Jackson, J., Jones, M.H., Bousso,

However, a second study reported in 1997, concluded that detector canines alerted to the methyl benzoate and not to pharmaceutical-grade cocaine. The same study also concluded that because methyl benzoate is volatile, its presence on "innocently" contaminated currency would be too low a level to cause an alert by a detector canine.[10] In 1999 the same authors again studied the issue. They again state that detector canines alert to methyl benzoate and not to pure, pharmaceutical-grade cocaine. This time however, it states that 1 nanogram per second of odor diffusion is needed to obtain an alert.[11]

10. That there are two major aspects to consider based on my review of the documents and testimony in this case. The first is the scientific concern of the lack of quality control by the canine handler and other agents. The scientific possibility of a false alert due to cross contamination is real in this actual case. Testimony provided by the agents stated that the area where the search was conducted was in the general offices of the Amtrak Police [direct testimony of Officer King P.33]. The actual room was referred to as the roll call area [direct testimony of Officer King P.11 and Amtrak Police Officer Romano P.199].

M, T., and Petrousky, J.A., Canine Olfactory Sensitivity to Cocaine hydrochloride and Methyl Benzoate, *Proceedings SPIE,* **2937**:19 (1996).
[10] Furton, F.G., Hsu,Y., Luo, T., Alvarez, N., and Lagos, P., Novel Sample Preparation methods and Field Testing procedures used to Determine the Chemical Basis of Cocaine detection by Canines, *Proceedings SPIE,* **2941** (1997).
[11] Furton, F.G., Hsu,Y., Luo, T., Norelus, A., and Rose, S., Field and Laboratory Comparison of the Sensitivity and Reliability of Cocaine Detection on Currency using Chemical Sensors, Humans, K-9s and SPME/GC/MS/MS Analysis, *Proceedings SPIE,* **2941** (1999).

11. That it is clear that persons and suspects involved in all crimes are brought to this area. The testimony indicates that drug cases are processed in this area and over one hundred (100) money seizures have occurred [direct testimony of Task Force Agent Terry P.135]. There is no indication that the area is cleaned other than routine janitorial procedures. There is no indication that the agents even considered the possibility of a false alert. [direct testimony of Officer King P.14 and Task Force Agent Terry P.85]. There are two points where cross contamination could occur. The first time was when the case was opened prior to the canine alert. This introduces the possibility that the currency or the case itself was contaminated in the Amtrak Police Office. This would, of course, require that the desk where it was opened had traces of cocaine on it or that cocaine is floating in the atmosphere in that general area. The second time was when the canine search was conducted. Drugs of all types are introduced into the area as a course of normal enforcement [direct testimony Task Force Agent Terry P.88], while only routine janitorial service is provided. The area is not a controlled environment and is not kept laboratory clean. If the detector canine has a highly sensitive nose the question is what is causing the alert.

12. That this failure to have better conditions for the dog sniff creates the question in the scientific community: Is it the currency or the room?

13. That the handler should have taken precautions by first allowing the canine to search the area without the currency being present. If the canine does not alert, then the handler and his canine could leave the area and agents could then "hide" the currency. If the canine always alerts to the currency [direct testimony of Task Force Agent Terry

P.135] and no quality control is maintained, the scientific concern is that the room itself or the general area where the case was placed causes the alert, not the currency. The procedure employed casts doubt on the significance of the canine sniff.

14. That the second scientific concern is the general contamination of currency. The studies indicate that there is a real and widespread contamination of the currency of the United States and many other countries. Each of the scientific researchers in the studies considered the level of contamination to be significant. The studies are all scientifically consistent with each other. The currency in this case may well be general circulation, contaminated currency. In this case, according to the statements and reports of the agents, since that actual currency was not retained, there were 4,665 actual banknotes, of which 4,326 are $20 banknotes. Since the 1998 Negrusz study, several other studies have found that denominations of $20 and $50 banknotes have a consistently higher percentage of contamination. The studies presented here and the others listed in Exhibit B clearly expect that detector canines could alert to legal, innocent, general circulation currency. In the 1985 unpublished Angelos study by the affiant, the belts of the high speed sorters in the U.S. Federal Reserve district bank were contaminated with cocaine. In a more recent 2003 published British study the researcher used blank paper the size of banknotes that were 'counted' in banks in England and Wales and subsequently analyzed. Based on the study the authors state:

> This study has shown that the widespread occurrence of nanogram amounts of cocaine on banknotes is, at least in part, due to transfer by counting machines. To a lesser degree, cocaine may be transferred by

hand counting.[12]

15. That the only studies confident that a detector canine will only alert to currency involved in the drug 'trade' are the two Furton studies. Those studies ignored the previous scientific work as limited, and only considered the 1989 Canadian Hudson study where it found Canadian currency to be contaminated with an average of 10 nanograms of cocaine. The Furton studies calculate that based on that level of trace contamination, a detector canine will not alert. Of course, the scientific studies that were ignored and subsequent studies have determined significantly higher levels cocaine contamination. The 1997 Furton study calculated that a detector canine:

> ...threshold level of detection of cocaine for the canines as tested is greater than 1 gram (containing <0.001% methyl benzoate impurity) with consistent threshold level of methyl benzoate of around 0.01 grams. (see footnote #10 p.62)

16. That the calculations make two assumptions. The first is that methyl benzoate is an impurity found at a low level of less than 0.001%. Methyl benzoate is not an impurity; it is a continually generated breakdown component of the cocaine as shown in the 1996 Dejarme study.

17. That the second assumption is that methyl benzoate evaporates quickly. The 1997 Furton study indicates that methyl benzoate placed on the banknote evaporated while the cocaine remained relatively unchanged. In fact, the percentage of weight increased, indicating that the cocaine gained weight. This is totally possible as cocaine is considered slightly hygroscopic, which means it will absorb water from the air. As

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[12] Carter, J.F., Sleeman, R., and Parry, J., The Distribution of Controlled Drugs

determined in the 1996 Dejarme study even a low 2% relative humidity will cause cocaine to breakdown and release a small amount of methyl benzoate. The 1996 Oyler and 2003 Carter studies both indicate that the crystals of cocaine are trapped within the fibers of the currency. Furton confirmed that the actual cocaine is stable and will stay on the banknote. The cocaine will slowly breakdown and release methyl benzoate. Therefore, I hold the opinion to a reasonable degree of scientific certainty that Furton's argument: that if the detector canine alerted the currency must be recently involved in the drug trade because the methyl benzoate will evaporate is not scientifically valid. Nor is the conclusion based upon a reasonable degree of scientific certainty.

18. That the currency in this case may be innocent, general circulation contaminated currency. The second Furton 1999 study continues to use the 10 micrograms per banknote, which is 1000 times greater than the base level of the Hudson study, the only study accepted by Furton, and the simple evaporation as in the previous study. Which does not account for the replenishment of methyl benzoate by cocaine breakdown. (see paragraphs 16 and 17)

19. That this study considerably lowers the detector canine alert threshold. The original 0.01 grams or 10 micrograms was changed to 1 to 10 micrograms. The study also changes the threshold amount of cocaine needed for an alert from 1 gram or 1000 milligrams to that of 500 milligrams of cocaine needs to be on the banknote for a detector canine alert. This is, of course, 50,000 times higher than the standard value of 10 microgram per banknote.

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on Banknotes via Counting Machines, *Forens. Sci. Intnl.*, **132** (2003).

20. That the calculations are not correct. A banknote with 500 milligrams of cocaine with 0.02% methyl benzoate would be 0.1 milligrams or 100 micrograms of methyl benzoate. This is 10 to 100 times greater than the threshold reported. Furton's adds to the calculation the 90% loss of methyl benzoate to obtain the 10 micrograms. This is again based on the faulty assumption that methyl benzoate is an impurity. It does not consider that methyl benzoate is a continually generated breakdown component of the cocaine on the banknotes as shown in the 1996 Dejarme study.

21. That it should also be noted that 500 milligrams is a half a gram. That amount of any white powder is visible to the unaided eye. Considering that a United States banknote's weight is about 0.93 grams, it would be covered with white powder equal to half its weight. Or in effect a banknote covered with the powder of a crushed aspirin tablet.

22. That the agents did not notice any powder on the currency in this case. Nor did they notice any powder in the briefcase [direct testimony Amtrak Police Officer Romano P.194].

23. That detector canines do not need a visible amount of cocaine to alert.

> ...are capable of detecting low levels of cocaine hydrochloride and methyl benzoate. In the present study, the detection capabilities of the dog surpassed the detection limits of the analytical instruments used in characterizing the output of the vapor generation devices. (see footnote #9 p.225)

24. That in this case neither the currency nor the case was subjected to a scientific analysis in a laboratory, to confirm the presence of cocaine or to determine the amount of cocaine actually on the banknotes. Additionally, the actual 4665 banknotes are not

available to be sent to any laboratory. All we have is the detector canine alert with the presumption that such an alert is proof of a violation of the statute. Title 21 Chapter 13 Subchapter I Part E Section 881 (a)(6) provides for the forfeiture of moneys when:

> a. …furnished or intended to be furnished by any person in exchange for a controlled substance or listed chemical…
> b. …all proceeds traceable to such an exchange…
> c. …used or intended to be used to facilitate any violation of the subchapter…

25. That I hold the opinion to a reasonable degree of scientific certainty, there is no doubt that the simple alert of the canine cannot show intended use of the currency. It is also doubtful that any scientific analysis would be helpful. A canine alert does not provide sufficient scientific evidence to meet the preponderance of the evidence required by either the first (a) or third (c) element set forth above, or criteria of the statute. And the second element (b), could only be supported by the laboratory analysis indicating a large percentage of banknotes with high amounts of cocaine.[13] The presumption that the detector canine alert is proof of the second criteria is not supported by the preponderance of the scientific literature.

26. That in reviewing United States of America *v.* Funds in the amount of Thirty thousand six hundred seventy dollars (403 F.3d 448), the US Court of Appeals relied on the 1999 Furton study when it calculated that there must be fifty thousand innocently contaminated bills to generate an alert. This is based on Furton's assumption of 10 micrograms per banknote contamination and the threshold amount 500 milligrams of

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[13] Ebejer, K.A., Winn, J., Carter, J.F., Sleeman, R., Parker, J., and Korber, F., The Difference between Drug Money and a "Lifetime's Savings", *Forens. Sci.*

cocaine to produce an alert. However, Furton's threshold is given as a range of 1 to 10 micrograms of methyl benzoate. At the 1 microgram level using Furton's calculation based on 10 micrograms per banknote contamination, five thousand bills would be required.

27. That the US Court of Appeals also relied on the Furton studies' error that methyl benzoate is an impurity that will evaporate, when it determined that innocently contaminated currency would not contain sufficient amounts of methyl benzoate to cause an alert unless it was recently in proximity to cocaine. This does not account for the replenishment of methyl benzoate by cocaine breakdown. (see paragraphs 16 and 17)

28. That my scientific opinions are based on the review of the government's Memorandum in support of its Motion for Summary Judgment and its Statement of Material Facts; as well as transcripts of testimony in a Motion to Suppress and the judge's opinion on the Motion to Suppress that were provided; and several other documents that consisted of various scientific articles, and reports. The alert by the detector canine on currency is insufficient to a reasonable degree of scientific certainty to prove the presence of cocaine in the context of a violation of the statute.

Intnl., **167** (2007).

29. Further, your affiant sayeth naught.

Sanford R Angelos

Sanford A. Angelos

Subscribed and Sworn to before
me this 4 day of November, 2010.

C. Joy Nogly

NOTARY PUBLIC

NOTARY PUBLIC OFFICIAL SEAL STATE OF ILLINOIS
C JOY NOGLY
MY COMMISSION EXPIRES
OCTOBER 30, 2013

Attachment A

Resume of Sanford A. Angelos

SANFORD A. ANGELOS **DEA Senior Forensic Chemist (Ret)**

EDUCATION

University of Illinois – Chicago	M.Ed. - Research Evaluation	(1985)
University of Illinois – Chicago	M.Sc. – Criminalistics	(1975)
University of Illinois – Chicago	B.Sc. – Chemistry	(1972)
High school -	Oak Park & River Forest High School	

WORK EXPERIENCE

Forensic Chemist Consultant	Aris Associates Ltd. (Independent Contractor for US DOJ-ICITAP and DOS-INL)	2/06 to present
Peer Review Panel Member	National Institute of Justice (US DOJ-OJP – BJA)	2/09 to present
Senior Forensic Chemist	U.S.-Drug Enforcement Administration	3/89 to 1/06
Visiting Forensic Chemist	Nat'l Inst. of Police Science, Tokyo, Japan	8/96 to 11/96
Forensic Chemist	U.S.-Drug Enforcement Administration	1/76 to 3/89
Associate Criminalist	Illinois Dept. of Law Enforcement	7/75 to 1/76
Teaching Assistant	UIC Dept. of Criminal Justice	9/74 to 6/75

INTERNATIONAL TRAINING **(see Appendix A, B)**

- 2010 Armenia (US DOS-INL) Georgia (US DOS-INL)
- 2009 Armenia (US DOS-INL)
- 2008 Thailand (US DOJ-ICITAP) Uzbekistan (US DOJ-ICITAP)
- 2007 Belize (US DOJ-ICITAP) Columbia (US DOJ-ICITAP)
- 2006 China (AAFS)
- 1996 Japan (US DOJ-DEA)

COMMUNITY SERVICE

- North Dearborn Association Treasurer (2009-2011)
- Local School Council Secretary (2009-2012)

MEMBERSHIPS **(see Appendix C)**

American Chemical Society	Member	1974
American Academy of Forensic Sciences	Fellow	1975
Clandestine Laboratory Investigating Chemists	In-Active	1990
Canadian Society of Forensic Sciences	Member	1982

TEACHING **(see Appendix D)**

Adjunct Faculty - Dept. of Science - Columbia College	1/84 to 1/90 & 9/06 to 12/08
Adjunct Faculty - Science Institute - Columbia College	8/92 to 6/06
Adjunct Faculty - Dept. of Chemistry -Roosevelt University	1/84 to 1/90
Adjunct Faculty - College of Education – UIC	1/82 to 1/88
Adjunct Faculty - Dept. of Criminal Justice – UIC	1/81 to 1/87

COURT TESTIMONY

- Over 300 times in State and Federal Courts
- Over 200 Clandestine Laboratory Investigations

CERTIFICATION

- DEA-Clandestine Laboratory Entry Team (CLET) [OSHA Certified 48 CFR 1910.120(q)]
- Bloodborne Pathogen Certified Instructor [Public Health Service]

PRESENTATIONS **(see Appendix E, A, B)**

- Over 45 presentations and workshops to the various organizations listed above

PUBLICATIONS **(see Appendix F)**

- Over 10 papers published

HONORS **(see Appendix G)**

Meritorious Service Award	American Academy of Forensic Sciences 2009
Exceptional Performance	DEA 1999; 1997; 1996; 1995
Research Award for Foreign Specialists	Japanese Government 1996

APPENDIX A – INVITED – GUEST PRESENTATIONS

(Note Presentations prior to 1/2000 not included)

AUGUST 2010 **Penn State – Forensic Science Lecture Series**
State College, Pennsylvania
- Forensic Science the Real CSI

April 2010 **Thermo Scientific Webinar**
Madison Wisconsin
- Illicit Drug Analysis using FT-IR with Mixture Searching

December 2007 **St. Johns College Forensic Seminar**
Belize City, Belize
-The Role Forensics in Law Enforcement

March 2003 **Michigan Science Teachers Association**
50th Annual Meeting
-The Use of Forensic Sciences in Teaching Science

April 2003 **Central Research and Creative Accomplishment Symposium**
Central Missouri State University
-Analysis of Controlled Substances

APPENDIX B – WORKSHOP PRESENTATIONS

September 2010	**National Forensic Bureau (Tbilisi, Georgia)** Presenter – Drug Analysis Infrared Spectroscopy
September 2010	**National Bureau of Expertise Forensic Section (Yerevan, Armenia)** Presenter –Drug Analysis Practical Infrared Spectroscopy and Gas Chromatography
June 2010	**National Forensic Bureau (Tbilisi, Georgia)** Presenter –Drug Analysis Liquid Chromatography
May 2010	**National Bureau of Expertise Forensic Section (Yerevan, Armenia)** Presenter –Drug Analysis Infrared Spectroscopy
December 2009	**National Bureau of Expertise Forensic Section (Yerevan, Armenia)** Presenter –Drug Analysis Wet Chemical Techniques
July 2009	**Science Workshop for Science Teachers (Chicago, Illinois)** **Visualization: The Future of Learning** Presenter -Forensic Sciences for Educators
August 2008	**Central Institute for Forensic Science Laboratory (Bangkok, Thailand)** Presenter- Gas Chromatography-Mass Spectrometry of Explosive Residue
August 2008	**Royal Thai Police Forensic Laboratory (Bangkok, Thailand)** Presenter- Drug and Instrumental Analysis
July 2008	**Science Workshop for Science Teachers (Chicago, Illinois)** **Visualization: The Key to the Future of Learning** Presenter -Forensic Sciences for Educators
April 2008	**Uzbekistan Ministry of Health Laboratory (Tashkent, Uzbekistan)** Presenter- Gas Chromatograph-Mass Spectrometry
December 2007	**Belize National Forensic Science Service (Belize City, Belize)** Presenter- Use of Gas Chromatograph-Mass Spectrometry in Drugs Analysis
July 2007	**Science Workshop for Science Teachers (Chicago, Illinois)** Presenter -Forensic Mysteries as a Way of Teaching
March 2007	**Columbian Joint Forensic Laboratory Seminar (Bogotá, Columbia)** Presenter- Designer Drugs Analysis -Methamphetamine and MDMA
November 2006	**2006 Police and Science International Forum (Hangshou, China)** Presenter- Clandestine Methamphetamine Laboratories
February 2005	**American Academy of Forensic Sciences Annual Meeting** Chair –Analysis of Samples from Clandestine Methamphetamine Laboratories

APPENDIX B – WORKSHOP PRESENTATIONS (Continued)

October 2004	**Southwestern Association of Forensic Scientists Annual Meeting** Chair –Clandestine Laboratory Production Capabilities Presenter -GC Quantitation & Validation Methodology
March 2004	**Michigan Science Teachers Association Annual Meeting** Presenter -Forensic Mysteries as a Way of Teaching
February 2004	**American Academy of Forensic Sciences Annual Meeting** Presenter -Drug Enforcement Administration – Forensic Drug Chemist Workshop
February 2004	**American Academy of Forensic Sciences Annual Meeting** Co-Chair –Bubble Bubble Boom Fires and Explosions in Clandestine Drug Laboratories
October 1995	**Midwestern Association of Forensic Scientists** Analysis of *d*,*l*-Methamphetamine
February 1992	**American Academy of Forensic Sciences Annual Meeting** GC/IRD/MSD Forensic Applications
February 1989	**American Academy of Forensic Sciences Annual Meeting** MACRO Programming for HP ChemStation

APPENDIX C - PROFESSIONAL AFFILIATIONS

AMERICAN ACADEMY OF FORENSIC SCIENCES

Local Arrangements Chair [a]	(2011)
By-laws Committee Member [a]	(1997-2011)
2007 Criminalistics Section Program Co-Chairman [s]	(2006)
Criminalistics Section's AdHoc Membership Committee	(2004-2005) Chair (2009-2012)
Criminalistics Section's Historian	(1995-1998)
Criminalistics Section's Award Committee	(1993-1997)-Chairman (1993)
Chairman of the AdHoc Proceedings Committee [a]	(1992-94)
Chairman - Criminalistics Section	(1992)
Nominating Committee [a]	(1992)
Council [a]	(1991-1992)
Membership Committee [a]	(1991-1992)
Secretary - Criminalistics Section	(1991)
1991 Criminalistics Section Program Chairman	(1990)
Member of the AdHoc Publication Committee [s]	(1982)
Chairman of the Criminalistics Section Planning Committee	(1987-89)

[a] Academy position [s] Criminalistics Section position

JOURNAL OF FORENSIC SCIENCES

Editorial Review Board	(1985-2002)

FORENSIC SCIENCES FOUNDATION

Student Affiliate Scholarship Committee Chair	(2009-2011)
Emerging Forensic Scientist Award Committee	(2010)

INTERNATIONAL ACADEMY OF FORENSIC SCIENCES

2008 Drugs of Abuse Section Program Chairman	(2007-2008)

AMERICAN CHEMICAL SOCIETY (Chicago Section)

Distinguish Service Award Committees (Chair 2006)	(2002-2006)
Treasurer	(1998-2000)
Policy – Bylaw	(1998-2002)
Awards	(1998-1999)
Member of the Board of Directors	(1984-1995; 1996-1998; 2000-2002)
Chairman of the Professional Relations Committee	(1990-91; 1995-96)
Program Co-Chair	(1995-1997)
Past-Chairman of the Section	(1994-95)
Chairman of the Section	(1993-94)
Chairman-Elect of the Section	(1992-93)
Chairman of the Environmental Health & Safety Committee	(1987-1989)
Chairman of the W. Gibbs Arrangement Committee	(1985)
Chairman of the House Committee	(1984)
CHEMICAL BULLETIN	
Co-Editor	(1999-2001)
Editorial Board	(1982-1997)
Editor	(1987-1989)

APPENDIX C - PROFESSIONAL AFFILIATIONS (Continued)

MIDWESTERN ASSOCIATION OF FORENSIC SCIENTISTS

Criminalistics Coordinator	(1985)
Member of the Executive Board	(1981-1983)
Meeting Program Coordinator	(1982)
MAFS BULLETIN	
Editor	(1981-1983)

COUNCIL OF FORENSIC SCIENCE EDUCATORS

Secretary -Treasurer	(1997-2002)
Interim Secretary-Treasurer	(1996)

APPENDIX D - ACADEMIC POSITIONS

COLUMBIA COLLEGE

SCIENCE and MATHEMATICS DEPARTMENT

56-2170-01SMW LifeSavers or Killers: The Story of Drugs
56-2749-01SM Scientific Investigation: Sherlock Holmes to the Courtroom
Various terms between January 1984 to June 1991
56-1280-01/02 Crime Lab Chemistry
Various terms between September 2006 to January 2009

SCIENCE INSTITUTE

60-4250-01SMW Crime Lab Chemistry
Various terms between January 1993 to June 2006

UNIVERSITY OF ILLINOIS - CHICAGO

DEPARTMENT OF CRIMINAL JUSTICE

CrJ 200 Criminalistics
CrJ 291 Introduction to Forensic Sciences
CrJ 314 Criminalistics Analytical Laboratory I
CrJ 315 Criminalistics Analytical Laboratory II
CrJ 460 Forensic Sciences Laboratory I
CrJ 461 Forensic Sciences Laboratory II
CrJ 464 Forensic Sciences Special Topics
Various terms between January 1981 to January 1987

COLLEGE OF EDUCATION

CIE 309 Consumer Drug Educations
CIE 310 Drug Evaluations
Various terms between January 1982 to January 1989

ROOSEVELT UNIVERSITY

CHEMISTRY DEPARTMENT

CHEM 311-10 Introduction to Forensic Sciences
CHEM 312-10 Forensic Drug Chemistry
CHEM 370-10 Forensic Chemistry

SOCIOLOGY DEPARTMENT

SOC 355-10 Criminology and Forensic Science
Various terms between January 1984 to August 1991

APPENDIX E - PRESENTATIONS

FEB 2010 AMERICAN ACADEMY OF FORENSIC SCIENCES
- Methamphetamine: Peanut Butter to Ice
- Clandestine Laboratory Capability: Actual *vs.* Theoretical

AUG 1999 INTERNATIONAL ASSOCIATION OF FORENSIC SCIENCES
-Methamphetamine by the Birch Reduction

FEB 1999 AMERICAN ACADEMY OF FORENSIC SCIENCES
-Production Capabilities of Clandestine Methamphetamine Laboratories

FEB 1998 AMERICAN ACADEMY OF FORENSIC SCIENCES
-Lithium-Ammonia Reduction of Pseudoephedrine to Methamphetamine

AUG 1996 INTERNATIONAL ASSOCIATION OF FORENSIC SCIENCES
-An Unsuccessful Clandestine Synthesis of Amphetamine
-Clandestine Synthesis of Fentanyl
-Clandestine Manufacture of Methadone

FEB 1996 AMERICAN ACADEMY OF FORENSIC SCIENCES
-Sodium-Ammonia Reduction of Ephedrine to Methamphetamine
-Analysis of Samples 4-Bromo-2,5-Dimethoxyphenethylamine (Nexus) an Analogue of 4-Bromo-2,5-Dimethoxyamphetamine (DOB)

OCT 1995 MIDWESTERN ASSOCIATION OF FORENSIC SCIENTISTS
-An Unsuccessful Clandestine Synthesis of Amphetamine
-Clandestine Synthesis of Fentanyl

AUG 1995 AMERICAN CHEMICAL SOCIETY
- Overview of Chemistry in the Forensic Sciences.
- Use of Forensic Sciences in Chemical Education

FEB 1994 AMERICAN ACADEMY OF FORENSIC SCIENCES
-Clandestine Synthesis of Fentanyl

SEPT 1993 CLANDESTINE LABORATORY INVESTIGATING CHEMISTS ASSOCIATION
-An Unsuccessful Clandestine Synthesis of Amphetamine

FEB 1993 AMERICAN ACADEMY OF FORENSIC SCIENCES
-An Unsuccessful Clandestine Synthesis of Amphetamine

AUG 1993 AMERICAN CHEMICAL SOCIETY
-Use of Gas Chromatography/Mass Spectrometry (GC/MS) in Non-science Major Course Laboratory Experiments Instrumentation of a Forensic Laboratory

FEB 1992 AMERICAN ACADEMY OF FORENSIC SCIENCES
-Clandestine Manufacture of Methadone

OCT 1990 INTERNATIONAL ASSOCIATION OF FORENSIC SCIENCES
-Synthesis of Amphetamine from Toluene
-An Investigation of Phenyl-2-Propanone Reaction Mechanisms

FEB 1990 AMERICAN ACADEMY OF FORENSIC SCIENCES
-Optimizing FT-NMR Pulse Patterns for Quantitation Measurements
-NMR Quantitation of Methamphetamine and Ephedrine Mixtures

OCT 1989 MIDWESTERN ASSOCIATION OF FORENSIC SCIENTISTS
-Automated Sampling for Gas Chromatography and for a Mass Selective Detector
-An Investigation of Phenyl-2-Propanone Reaction Mechanisms

FEB 1989 AMERICAN ACADEMY OF FORENSIC SCIENCES
-NMR Examination of Cocaine and Heroin
-NMR Analysis of PCP Analogues

OCT 1988 CANADIAN SOCIETY OF FORENSIC SCIENCES
-Automated Analysis on High Pressure Liquid Chromatography, Precision, Accuracy, and Linearity
-Automated Analysis on Capillary Gas Chromatography, Precision, Accuracy, and Linearity
-Automated Analysis on a Mass Selective Detector

OCT 1988 MIDWESTERN ASSOCIATION OF FORENSIC SCIENTISTS
-Automated Instrumental Analysis

FEB 1988 AMERICAN ACADEMY OF FORENSIC SCIENCES
-Automated Analysis on High Pressure Liquid Chromatography, Precision, Accuracy, and Linearity
-Automated Analysis on Capillary Gas Chromatography, Precision, Accuracy, and Linearity
-Automated Analysis on a Mass Selective Detector
-Synthesis of Amphetamine from Toluene
-The Analysis of an Analogue of Methaqualone

AUG 1987 INTERNATIONAL ASSOCIATION OF FORENSIC SCIENCES
-Clandestine Manufacture of 4-Bromo-2,5-Dimethoxyamphetamine
-A Gas Chromatography/Mass Spectrometry System for the Identification of Clandestinely Produced Phencyclidine Preparations
-Quantitation and Identification of Pharmaceutical Preparation by Nuclear Magnetic Resonance

FEB 1987 AMERICAN ACADEMY OF FORENSIC SCIENCES
-Potential Safety Hazards in a Forensic Laboratory
-Identification of Clandestine Phencyclidine Mixtures by Capillary Gas Chromatography/Mass Spectrometry
-An Investigation of Phenyl-2-Propanone Reaction Mechanisms

FEB 1986 AMERICAN ACADEMY OF FORENSIC SCIENCES
-Distinguishing the Optical Isomers of Propoxyphene by Infrared Spectroscopy
-A Statistical Evaluation of Research Published in The *Journal of Forensic Sciences*

FEB 1985 AMERICAN ACADEMY OF FORENSIC SCIENCES
-An Evaluation of Research Attitudes and Productivity of Forensic Science Higher Education Faculty
-The Role of the Forensic Chemist in Clandestine Laboratory Investigations, Seizures and Prosecutions

JAN 1985 AMERICAN CHEMICAL SOCIETY
-Clandestine Manufacture of 4-Bromo-2,5-Dimethoxyamphetamine

OCT 1984 AMERICAN CHEMICAL SOCIETY (CHICAGO-SAFETY SYMPOSIUM)
-Liability and the Drug Laws

FEB 1984 AMERICAN ACADEMY OF FORENSIC SCIENCES
-Attitudes of Criminalists Towards The *Journal of Forensic Sciences*: A Survey Analysis
-The Synthesis of P-2-P from Allybenzene
-Clandestine Manufacture of 4-Bromo-2,5-Dimethoxyamphetamine

FEB 1983 AMERICAN ACADEMY OF FORENSIC SCIENCES
-Analysis of a "Simple" Synthesis of P-2-P from Its Alcohol

FEB 1982 AMERICAN ACADEMY OF FORENSIC SCIENCES
-The Analysis of P-2-P Synthetic Mixtures Obtained from Clandestine Laboratories
-Quantitation and Identification of Pharmaceutical Preparations by Nuclear Magnetic Resonance
-Characteristics of Forensic Science Faculty Within Criminal Justice Higher Education Programs

MAY 1981 MIDWESTERN ASSOCIATION OF FORENSIC SCIENTISTS
-Quantitation and Identification by Nuclear Magnetic Resonance

FEB 1981 AMERICAN ACADEMY OF FORENSIC SCIENCES
-Identification and Quantitation of Multiple Barbiturate Preparations By Nuclear Magnetic Resonance
-A Comparative Study on the Use of Shift Reagents in the NMR Determination of Methamphetamine and Amphetamine Enantiomers

FEB 1980 AMERICAN ACADEMY OF FORENSIC SCIENCES
-Identification and Quantitation of Barbiturates by Nuclear Magnetic Resonance

NOV 1979 MIDWESTERN ASSOCIATION OF FORENSIC SCIENTISTS
-Distinguishing The Optical Isomers of Propoxyphene by Infrared Spectroscopy

OCT 1978 MIDWESTERN ASSOCIATION OF FORENSIC SCIENTISTS
-The Isolation and Identification of Precursors and Reaction Products In The Clandestine Manufacture of Methaqualone and Mecloqualone

SEPT 1977 AMERICAN CHEMICAL SOCIETY
-Identification of Some Chemical Analogues and Positional Isomers of Methaqualone

APPENDIX E – PRESENTATIONS (Continued)

FEB 1977 AMERICAN ACADEMY OF FORENSIC SCIENCES
-The Isolation and Identification of Precursors and Reaction Products In The Clandestine Manufacture of Methaqualone and Mecloqualone

OCT 1976 MIDWESTERN ASSOCIATION OF FORENSIC SCIENTISTS
-Identification of Some Chemical Analogues and Positional Isomers of Methaqualone

MAY 1976 MIDWESTERN ASSOCIATION OF FORENSIC SCIENTISTS
-A Study of the Criminalistic Identification of Lipstick Stains

APPENDIX F – PUBLICATIONS-Journal

JOURNAL OF FORENSIC SCIENCES Volume 26, Number 4, Page 656
*Approaches To Drug Sample Differentiation II: Nuclear Magnetic Resonance Spectrometric Determination of Methamphetamine Enantiomers

JOURNAL OF FORENSIC SCIENCES Volume 26, Number 4, Page 793
*Identification of Some Chemical Analogues and Positional Isomers of Methaqualone

JOURNAL OF FORENSIC SCIENCES Volume 28, Number 3, Page 552
*Characteristics of Forensic Science Faculty within Criminal Justice Higher Education Programs

JOURNAL OF FORENSIC SCIENCES Volume 29, Number 4, Page 1187
*A Clandestine Approach To The Synthesis of P-2-P From Phenylpropenes

JOURNAL OF FORENSIC SCIENCES Volume 30, Number 1, Page 269
*An Evaluation of Criminalists' Attitudes Towards The *Journal of Forensic Sciences*

JOURNAL OF FORENSIC SCIENCES Volume 30, Number 4, Page 1022
*The Isolation and Identification of Precursors and Reaction Products In The Clandestine Manufacture of Methaqualone and Mecloqualone

JOURNAL OF FORENSIC SCIENCES Volume 35, Number 6, Page 1297
*The Identification of Precursors, Impurities, and By-Products In Clandestinely Produced Phencyclidine Preparations

JOURNAL OF FORENSIC SCIENCES Volume 36, Number 2, Page 358
*The Identification and Quantitation of Pharmaceutical Preparations By Nuclear Magnetic Resonance Spectroscopy

JOURNAL OF FORENSIC SCIENCES Volume 38, Number 2, Page 455
*The Structural Identification of a Methyl Analog of Methaqualone Via 2-Dimensional NMR Techniques

JOURNAL OF CHEMICAL EDUCATION June 1996 Volume 73, Number 6, Page 565
*Use of Gas Chromatography-Mass Spectroscopy (GC-MS) in Nonscience Major Course Laboratory Experiments

APPENDIX F – PUBLICATIONS-Other

U.S. D.E.A. - MICROGRAM Volume XXII, Number 3, Page 38
*Hewlett Packard Programming for the MSD Chem Station: Part I. Standard Search & Print Program

U.S. D.E.A. - MICROGRAM Volume XXII, Number 3, Page 41
*Perkin Elmer Obey Programming for FT-IR with CDS-3 Software: Part I. Print Programs

U.S. D.E.A. - MICROGRAM Volume XXII, Number 10, Page 194
*Perkin Elmer Obey Programming for FT-IR with CDS-3 Software: Part II. Automated Scan-Save-Print Programs

CRIMINALISTICS: AN INTRODUCTION TO FORENSIC SCIENCES - LAB MANUAL (1989)
R. SAFERSTEIN, EDITOR <u>EXPERIEMENT #27 PAGE 217</u>
"Determination of Lipstick Dyes by Thin-Layer Chromatography"

APPENDIX F – PUBLICATIONS-Proceedings

PROCEEDINGS OF THE AMERICAN ACADEMY OF FORENSIC SCIENCES *Volume* 16, Number 16
* Methamphetamine: Peanut Butter to Ice

PROCEEDINGS OF THE AMERICAN ACADEMY OF FORENSIC SCIENCES *Volume* 16, Number 16
***** Clandestine Laboratory Capability: Actual *vs.* Theoretical

PROCEEDINGS OF THE **2006 POLICE AND SCIENCE INTERNATIONAL FORUM**
* Clandestine Methamphetamine Laboratories Legal Perspectives and Analytical Procedures in the United States (in Chinese translation)

PROCEEDINGS OF THE AMERICAN ACADEMY OF FORENSIC SCIENCES *Volume* 2, Number 2
*Sodium-Ammonia Reduction of Ephedrine to Methamphetamine

PROCEEDINGS OF THE AMERICAN ACADEMY OF FORENSIC SCIENCES *Volume* 2, Number 2
*Analysis of Samples 4-Bromo-2,5-Dimethoxyphenethylamine (Nexus) an Analogue of 4-Bromo-2,5-Dimethoxyamphetamine (DOB)

PROCEEDINGS OF THE AMERICAN ACADEMY OF FORENSIC SCIENCES *Volume* 4, Number 4
*Lithium-Ammonia Reduction of Pseudoephedrine to Methamphetamine

PROCEEDINGS OF THE AMERICAN ACADEMY OF FORENSIC SCIENCES *Volume* 5, Number 5
*Production Capabilities of Clandestine Methamphetamine Laboratories

Current Topics in Forensic Science
PROCEEDINGS OF THE 14th MEETING OF THE INTERNATIONAL ASSOCIATION OF FORENSIC SCIENCES Volume 2, page 310
*An Unsuccessful Clandestine Synthesis of Amphetamine

Current Topics in Forensic Science
PROCEEDINGS OF THE 14th MEETING OF THE INTERNATIONAL ASSOCIATION OF FORENSIC SCIENCES Volume 2, page 312
*Clandestine Synthesis of Fentanyl

Current Topics in Forensic Science
PROCEEDINGS OF THE 14th MEETING OF THE INTERNATIONAL ASSOCIATION OF FORENSIC SCIENCES Volume 2, page 374
*Clandestine Manufacture of Methadone

Current Topics in Forensic Science
PROCEEDINGS OF THE 15th MEETING OF THE INTERNATIONAL ASSOCIATION OF FORENSIC SCIENCES, page 61
*Methamphetamine by the Birch Reduction

APPENDIX G – AWARDS and HONORS

(Note Awards prior to 1/1995 not included)

2009 **American Academy of Forensic Sciences Criminalistics Section**

- Meritorious Service Award

2004 **U.S. Department of Justice Drug Enforcement Administration**

- Certificate of Appreciation Award

2003 **U.S. Department of Justice Drug Enforcement Administration**

- Special Act or Service

1999 **U.S. Department of Justice Drug Enforcement Administration**

- Exceptional Performance

1998 **Columbia College of Chicago**

- Teacher of the Year (Adjunct Faculty)

1997 **U.S. Department of Justice Drug Enforcement Administration**

- Exceptional Performance

1996 **Japanese Government National Police Agency**

- Research Award for Foreign Specialists

U.S. Department of Justice Drug Enforcement Administration

- Exceptional Performance

Chicago Area Technological Societies

- Award of Merit

1995 **U.S. Department of Justice Drug Enforcement Administration**

- Exceptional Performance

American Chemical Society

- Appreciation Award
- Appreciation Award (Second Award)

Attachment B

List of Articles and Reports

Articles and Reports Cited

Angelos, S.A., Unpublished Report "Trace Analysis of U.S. Currency" U.S. Drug Enforcement Administration, Forensic Science Section, (1985). **Copy attached**

Hudson, J.C., Analysis of Currency for Cocaine Contamination, *Can. Soc. Forens. Sci. J.*, **22**:2:203-218 (1989). **Copy attached**

Oyler, J., Darwin, W.D., and Cone, E.J., Cocaine Contamination of United States Paper Currency, *J. Analyical Toxicology,* **20:**4: 213-216 (1996). **Copy attached**

Negrusz, A., Perry, J.L., and Moore C.M., Detection of Cocaine on various Denominations of United States Currency, *J. Forens. Sci.*, **43**:3 (1998). **Copy attached**

Jenkins, A.J., Drug Contaminations of US Paper Currency, *Forens. Sci. Intnl.,* **121** (2001). **Copy attached**

Zuo, Y., Zhang, K., Wu, J., Rego, C., and Fitz, J., An Accurate and Nondestructive GC method for determination of Cocaine on US Paper Currency, *J. Separation Sci.,* **31** (2008). **Copy attached**

Zuo, Y., et.al., Unpublished presentation to the American Chemical Society. **ACS Press Release and Article attached**

Dejarme, L.E., Gooding, R.E., Lawhon, S.J., Ray, P., and Kuhlman, M.R., Formation of Methyl Benzoate from Cocaine hydrochloride under Different Temperatures and Humidies, *Proceedings. SPIE,* **2937:**19 (1996). **Copy attached**

Waggoner,L.P., Jonston, J.M., Williams, M., Jackson, J., Jones, M.H., BoussoM, T., and Petrousky, J.A., Canine Olfactory Sensitivity to Cocaine hydrochloride and Methy Benzoate, *Proceedings SPIE,* **2937:**19 (1996). **Copy attached**

Furton, F.G., Hsu,Y., Luo, T., Alvarez, N., and Lagos, P., Novel Sample Preparation methods and Field Testing procedures used to Determine the Chemical Basis of Cocaine detection by Canines, *Proceedings SPIE,* **2941** (1997). **Copy attached**

Furton, F.G., Hsu,Y., Luo, T., Norelus, A., and Rose, S., Field and Laboratory Comparison of the Senitivity and Reliability of Cocaine Detction on Currency using Chemical Sensors, Humans, K-9s and SPME/GC/MS/MS Analysis, *Proceedings SPIE,* **2941** (1999). **Copy attached**

Carter, J.F., Sleeman, R., and Parry, J., The Distribution of Controlled Drugs on Banknotes via Counting Machines, *Forens. Sci. Intnl.,* **132** (2003). **Copy attached**

Ebejer, K.A., Winn, J., Carter, J.F., Sleeman, R., Parker, J., and Korber, F., The Difference between Drug Money and a "Lifetime's Savings", *Forens. Sci. Intnl.,* **167** (2007). **Copy attached**

Articles and Reports Reviewed

Wimmer, K., and Schneider, S., Screening for Illicit Drugs on Euro Banknotes by LC-MS/MS, *Forens. Sci. Intnl*, Article in Press (2010). **Copy attached**

Felix, J., and Gardner, E.A., Cocaine Contamination of Paper Currency in Birmingham, Alabama, *Proceedings Am. Acad. Forens. Sci.*, (2009). **Student presentation Abstract attached**

Sleemam, R., Burton, I.F.A., Carter, J.F., and Roberts, D.J., Rapid Screening of Banknotes for the Presence of Controlled Substances by Thermal Desorption Atmospheric Pressure Chemical Ionization Tandem Mass Spectrometry, *The Analyst*, **124** (1999). **British Study confirms both Oyler and Hudson Copy attached**

Sleemam, R., Burton, I.F.A., Carter, J.F., Roberts, D.J., and Hulmston, P., Drugs on Money, *Anal. Chem*, June (2000) **Copy attached**

Jourdan, T.H., Veitenheimer, A., and Wagner, J.R., Exploration Of Cocaine Contamination of United States Currency – Continuing Studies, *Proceedings Am. Acad. Forens. Sci.*, (2010). **Abstract attached**

Heimbuck, C.A. and Bower, N.W., Teaching Experiment Design Using a GC-MS Analysis of Cocaine on Money: A Cross-Disciplinary Laboratory, *J. Chem. Ed.*, **79**:10 (2002). **Reviewed on-line**

Esteve-Turrillas, F.A., et al. Validated, non-destructive and environmentally friendly determination of cocaine in euro bank notes. *Journal of Chromatography A*, **1065,** (2005). **Reviewed on-line**

Xu, Y., et al. Field-amplified sample stacking capillary electrophoresis with electrochemiluminescence applied to the determination of illicit drugs on banknotes. *Journal of Chromatography A*, **1115** (2006). **Reviewed on-line**

Di Donato, E., Santos Martin, C.C., and De Martinis, B.S., Determination of cocaine in Brazilian currency by capillary gas chromatography/mass spectrometry. *QuimNova.* **30:**8 (2006). **Reviewed on-line**

Ebejer, K.A., et al., Factors influencing the contamination of UK banknotes with drugs of abuse. *Forens. Sci. Intnl,* **171** (2007). **Reviewed on-line**

Attachment C1

Angelos, S.A., Unpublished Report "Trace Analysis of U.S. Currency" U.S. Drug Enforcement Administration, Forensic Science Section, (1985).

12 JUL 1985

North Central Laboratory, ATL#5

Final Report of Project C-0033
(FFS: 940-02)

RICHARD S. FRANK, CHIEF, ATS
FORENSIC SCIENCES SECTION

Attached is the final report on project C-0033 entitled "Trace Analysis of U.S. Currency".

I recommend that this project be terminated in light of the results obtained by Forensic Chemist Angelos. I also support the recommendations made by Forensic Chemist Angelos and urge that the results of this project if deemed too sensitive to publish be given wide dissemination within DEA.

Original Signed by
BENJAMIN A. PERILLO

BENJAMIN A. PERILLO
Laboratory Chief

Attachment:

SAA:djg 7/11/85
ATL#5 FILE 940-02 PROJECT ATL#5
ATL#5 CHRON
ATL#5 RF
SAA
DJG

Sanford A. Angelos, Forensic Chemist
Thru: David W. Parmalee, Supervisory Chemist

Report on Trace Analysis of U.S. Currency

BENJAMIN A. PERILLO, LABORATORY CHIEF
NORTH CENTRAL LABORATORY, ATL65

Background

Within the past year numerous requests have been made, by both DEA and authorities outside of the agency, for assistance in the analysis of U.S. currency. The requests range from providing information to actual requests for analysis of samples. As a result, several FBI and DEA cases have been developed using the information obtained by extraction and identification of cocaine from U.S. currency. A recent High Times article cited that shredded U.S. currency from a Federal Reserve Bank was found to have traces of cocaine (1). Additionally, a Tampa newspaper article reports the finding of traces of cocaine on ten of eleven $20 bills tested (2). Finally, an expert witness for the defense, has testified that he found traces of cocaine in samples from seven major Miami banks (3). A project (C-0035) was initiated to determine the extent of cocaine contamination on U.S. currency supplied by the Federal Reserve Banks.

Experimental

The following procedure was used with all samples analyzed (4):

1. Samples were soaked with 100ml of chloroform for ≅ 2 minutes.

2. Recovery of 95 to 100ml of chloroform.

3. Reduction of volume to 10ml.

4. Back extraction with 0.1 normal sulphuric acid.

5. Retained aqueous phase made basic with ammonium hydroxide.

6. Extraction with 10ml of chloroform.

7. Evaporation of solvent to dryness.

8. Residue dissolved in 0.5ml methanol.

Blanks

The project was done in five separate phases and in each phase a glassware/solvent blank was taken. Although two of the blanks had a gray-green tint, they were all negative.

Instrumentation

A Finnigan 4500 gas chromatograph-mass spectrometer with a Incos data system was used to detect the presence of cocaine. The instrument was capable of detection of 100 nanograms of cocaine. The parameter are as follows: column 3% OV-101 6 foot; electron impact; 70 electron volts; at 230`C.

Phases I-V

The first phase was the analysis of six samples of shredded $50 dollar bills provided by the Chicago Federal Reserve Bank. These samples were randomly selected by bank personnel while processing the bills submitted by several banks from the Chicago area. See Table 1.

The second phase was the analysis of five samples of shredded $100 dollar bills provided by the Chicago Federal Reserve Bank. These samples were randomly selected by bank personnel while processing the bills. Both phase one and two samples were submitted by the same area banks. See Table 2.

The third phase was the analysis of five samples of shredded $50 dollar bills. Like those in phase one they were randomly selected from the processing of a batch of money from area banks. This is a different submission than phase one. See Table 3.

The fourth phase was the analysis of five samples of shredded $100 dollar bills. As were the samples of phase three, these randomly selected samples were submitted by area banks at the same time as those in phase three. See Table 4.

The final phase was the analysis of five belts from the high speed apparatus used to sort unfit money from that eligible to be released for general circulation. The belts were analyzed as one sample.

Results

Of the twenty-one shredded money samples submitted for analysis, seven were found to have traces of cocaine. One-third of a randomly selected sample is a significant argument that the general currency in circulation is contaminated with traces of cocaine. The amount of the cocaine detected ranged from 2.4 to 12.3 nanograms per bill.

The result of the analysis of the belts from the high speed sorting apparatus is positive for cocaine with an estimated 200 nanograms being detected. This result, is more significant than the finding of one third of the samples to be contaminated. The apparatus is used to count and sort fit from unfit U.S. currency prior to its circulation by the Federal Reserve Bank.

Conclusion

The results, from the samples received from the Chicago Federal Reserve Bank, confirms the presence of traces of cocaine on general circulation U.S. currency. Moreover, the results indicate that the Federal Reserve Bank itself may be contaminating the currency through the normal procedures used by the bank. The belts must be initially contaminated by the currency, then inturn the belts will contaminate "clean" currency. These results indicate the termination of the project as all aspects show that the forensic usefulness of trace analysis is at best limited.

Recommendation

1. The project be terminated.

2. That trace analysis of currency for general enforcement or seizure be stopped.

3. That trace analysis of currency be done only for limited special intelligence purposes.

4. That DEA discourage the use of trace analysis of currency by presenting and publishing the results in the scientific literature.

5. That seized, forfeited or abandoned monies that are possibly contaminated with any controlled substance be flagged for subsequent shredding by the Federal Reserve Bank.

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Can. Soc. Forens. Sci. J. Vol. 22. No 2 (1989)

ANALYSIS OF CURRENCY FOR COCAINE CONTAMINATION

J.C. HUDSON[1]

ABSTRACT

Currency is often seized in drug investigations and increasingly under Section 312 of the Criminal Code, Possession of Property Obtained By Crime. Analysis for cocaine on seized currency could provide important evidence when compared to representative or background currency samples from the offence area. In this study samples obtained from the Bank of Canada in Regina, Saskatchewan, were analyzed quantitatively by gas chromatography with nitrogen-phosphorus detection or gas chromatography/mass fragmentography (GC/MF). Cocaine was present at background levels of less than 10 nanograms per note. In comparison, case samples were grossly contaminated with cocaine in the range from 50 to over 1000 times the background levels determined for Sasktachewan.

RÉSUMÉ

Très souvent, dans le cadre d'une enquête sur les stupéfiants, on saisit de l'argent; pour ce faire, on se sert de plus en plus de l'article 312 du Code criminel (Avoir en sa possession des biens criminellement obtenus). L'analyse révélant la présence de cocaïne sur les billets saisis pourrait fournir une preuve des plus concluantes lorsqu'on les compare à des échantillons de monnaie représentative de la région où s'est produite l'infraction. Une analyse quantitative d'échantillons obtenus du Bureau régional de la Banque du Canada à Régina en Saskatchewan, effectuée par chromotographie gazeuse avec détection azote-phosphore ou par chromotographie gazeuse — fragmentation de masse (CG-FM), démontre une concentration de cocaïne de moins de 10 nanogrammes par billet. Par contre, les échantillons saisis étaient tellement contaminés par la cocaïne qu'ils montraient une concentration de 50 à 1000 fois supérieure à celle des billets de la Banque du Canada à Régina.

BACKGROUND

On occasion this laboratory has been asked to analyze samples of currency seized in connection with drug investigations for the presence of illicit drugs such as cocaine. In the past, this type of analysis has provided little significant information except that a particular drug was indeed present. This information has seldom been very useful, especially recently when reports in the U.S. media and elsewhere (1) have indicated that cocaine contamination on currency is widespread.

Previous laboratory experience with case currency samples has indicated that this study could only be done for basic drugs, notably cocaine, and only after the removal of acidic and neutral compounds (phthalates and ''finger'' components) by an appropriate solvent back extraction. Exceptions would be visually detectable contamination by, for example, stains from Cannabis preparations such as ''hash oil''.

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In order for this type of study to be meaningful, an understanding of the currency flow in a given geographical area must be known, and samples which are representative of currency in general circulation must be obtained.

Because potentially large samples of currency may be encountered in application to actual casework, the most meaningful information would be gained by analyzing samples in batches according to denomination. The cocaine levels determined per piece of currency from the case could then be compared to the results per note of samples taken from the general circulation (background samples) with the end purpose being to offer expert evidence on such a comparison to the courts.

With the above in mind, this study was undertaken to assess the feasibility of using gas chromatography (GC) with nitrogen-phosphorus detection (NPD) with and without internal standards, or gas chromatography/mass fragmentography (GC/MF) in the analysis of extracts of seized currency.

EXPERIMENTAL

Materials

Absolute ethanol (Consolidated Alcohols Ltd.), chloroform (BDH Chemicals, ethanol stabilized), ethyl acetate (BDH Chemicals), methanol (BDH Chemicals), hydrochloric acid (BDH Chemicals), sulfuric acid (Fisher Scientific), and sodium hydroxide (BDH Chemicals) were all reagent grade. Screw cap tubes, (Kimble, 15 mL, 16x125 mm) with foil lined caps (Kimble 74520) were used in the extractions. Centrifuge tubes (Kimble, 5 mL, 73785) were used in evaporating the solvent to dryness under nitrogen prior to reconstitution with ethyl acetate.

Standards

Drug standards (as their hydrochloric acid salts) were obtained from the Licensed Dealer, Toxicology Section, Central Forensic Laboratory, R.C.M. Police, Ottawa, Ontario, and verified by melting points or gas chromatography/mass spectrometry. Stock solutions were prepared at a concentration of 1 milligram (calculated as the free base) per millilitre in ethanol. Working standards were prepared by diluting the stock solutions to 10 nanograms per microlitre with ethanol. Drug standard solutions were stored at 4°C.

Appropriate amounts of the working standards were added to ten millilitres of chloroform. A standard curve was prepared over the 25 to 1000 nanogram per sample range. Integration values per nanogram of the closest standard were used to determine absolute amounts in the GC method. Linear regression analysis of the ratio of cocaine to bupivacaine peak height values versus cocaine concentration was used to obtain GC/MF quantitative results of analysis of the background samples. This curve was repeated for each study.

Instrumentation

Two Hewlett-Packard (HP) 5710A gas chromatographs (GC's), and a Hewlett-Packard 5880A gas chromatograph, each equipped with nitrogen-phosphorus specific detectors (NPD) were used in this study. (Note: Prior to this work the HP 5880A GC was equipped with a flame ionization detector (FID) and was used to produce Figure 2 under the conditions described below). The HP 5710A GC's were fitted with 0.53 mm I.D. fused silica columns (one 10 m, the other 30 m) coated with a 1.5 micron film of methyl silicone (DB-1). The HP 5710A GC's were programmed from 115°C to 290°C at 8°C/min. For both instruments the helium carrier gas flow was 20 mL/min. Flow rates for the detector

gases were 3 mL/min for hydrogen and 70 mL/min for air. Injector and detector temperatures were maintained at 250°C and 300°C, respectively. Injectors were packed column type converted for splitless injection on 0.53 mm capillary columns. The HP 5880A GC was fitted with a 15 m, 0.25 mm I.D. fused silica column, coated with a 0.25 micron film thickness of methyl silicone (DB-1), programmed at 10°C per minute from 130°C with a 1 minute hold, to 290°C with a 3 minute hold at the final temperature. The injector was a split/splitless type operated in the split mode at a ratio of 100 to 1. Injector and detector temperatures were 250°C and 300°C, respectively. Total analysis times were less than 20 minutes. Peak areas were determined using a Hewlett-Packard 3350 Laboratory Automation System (LAS).

The gas chromatograph/mass spectrometer (GC/MS) system was a Hewlett-Packard 5890 GC, fitted with a 30 m, 0.25 mm I.D. fused silica column, coated with a 0.25 micron film thickness of methyl silicone (DB-1), programmed at 10°C per minute from 130°C, with a 1 minute hold, to 290°C with a 3 minute hold at the final temperature. The injector was a split/splitless type operated in the splitless mode with a sweep or purge time of 0.5 minute. The GC was coupled to a Finnigan INCOS 50 Mass Spectrometer through a heated transfer line maintained at 290°C. The electron impact (EI) source was maintained at 170°C. Selected ion monitoring (SIM) of the 182 ion (cocaine) and the 140 ion (bupivacaine) was used in the quantitative determinations for the standard, background, and case extracts.

Extraction Procedure

The general procedure for extracting drugs from currency is outlined in Figure 1. In the background determinations on batches of 100 notes from each denomination, ethanol (300 mL in an evaporating dish) was used as the extraction solvent. Each note was held with tweezers, immersed and moved back and forth in the ethanol for five seconds. Each note was drained by contact with the side of the evaporating dish for an additional five seconds. The note was then placed on Benchkote (Whatman) laid out on benches or tables. When extracting samples of currency from drug investigations, a minimum of three millilitres of ethanol per note was used (eg. 300 mL for 100 notes). Latex examination gloves were used during the initial extraction procedure and were changed between denominations. The ethanol solution remaining (approximately 275 mL) after extracting a 100 note batch, was allowed to evaporate overnight. The residue was taken up in ten millilitres of chloroform and filtered through chloroform washed and silanized glass wool in a pasteur pipette to remove pieces of loose cellulose, dirt and dust. The chloroform filtrate was collected in a 15 mL screw cap tube. The internal standard, bupivacaine in ethanol, at a concentration of 10 nanograms per note, was added to the chloroform solution. This chloroform solution was extracted with 2 mL or 10% (v/v) sulfuric acid on a flat bed shaker (10 min). The tubes were centrifuged at 1500 RPM for five minutes. To permit a more complete recovery of the aqueous layer, one millilitre of water was added and the top acidic layer decanted into a second 15 mL tube. Chloroform (5 mL) was added, and tube was shaken for five minutes. The tube was then centrifuged and the chloroform extract containing acidic and neutral interfering components was removed and discarded using a pasteur pipette.

The acidic aqueous solution was made basic by the addition of 2 mL of 25% (w/v) sodium hydroxide. The tube was vortexed and five millilitres of chloroform were added. The tube was shaken for five minutes and centrifuged as described. The chloroform layer was removed and filtered through anhydrous sodium sulfate (50 mg) (in a pasteur pipette plugged with chloroform washed and silanized glass wool) into a 5 mL centrifuge tube. In order to prevent hydrolysis of cocaine to benzoylecgonine under basic conditions, the chloroform

```
                      CURRENCY SAMPLE
         immerse 5 sec ¦ in ethanol
                       ¦ drain, dry notes
                     ETHANOL
                       ¦ evaporate overnight
                   CHLOROFORM
                       ¦ add I.S.,H2SO4
    shake,centrifuge,¦ add water,decant
      -------------------------------
      ¦                            ¦
CHLOROFORM                    AQUEOUS (Acidic)
      ¦                            ¦ add chloroform
  DISCARD                     shake,¦ centrifuge,decant
            ------------------------
            ¦                         ¦
       CHLOROFORM              AQUEOUS (Acidic)
            ¦                     add ¦ NaOH,CHCl3
         DISCARD                shake¦ centrifuge
                                      ¦ decant
                      ------------------------
                      ¦                       ¦
              CHLOROFORM               AQUEOUS (Basic)
         evaporate ¦ N2                       ¦
          dissolve ¦ residue              DISCARD
                   ¦
             ETHYL ACETATE
                   ¦
        GC (1/20) or GC/MF (1/50)
```

Figure 1 Extraction/Separation Scheme

extraction was done as quickly as possible (preferably in less than twenty minutes) (2). One hundred microlitres of 1% concentrated hydrochloric acid in methanol (made fresh monthly) (3) was added to the chloroform prior to evaporation to dryness under nitrogen at room temperature. The residue was reconstituted with 20 microlitres of ethyl acetate. One microlitre injections were made on each gas chromatograph. The 20 microlitres were diluted to 50 microlitres for the GC/MS study again with 1 microlitre injected.

RESULTS AND DISCUSSION

Study Considerations

One of the first questions to considered in a study of this type was "Which drugs would you expect to encounter?" Analysis of currency samples using a similar extraction scheme prior to this work (Figure 2) indicated that detecting and quantitating low levels of basic drugs using GC's equipped with flame ionization detectors (FID) would be, at best, difficult on such a complex extract. Hence more specific (NPD or GC/MS) detectors would be required.

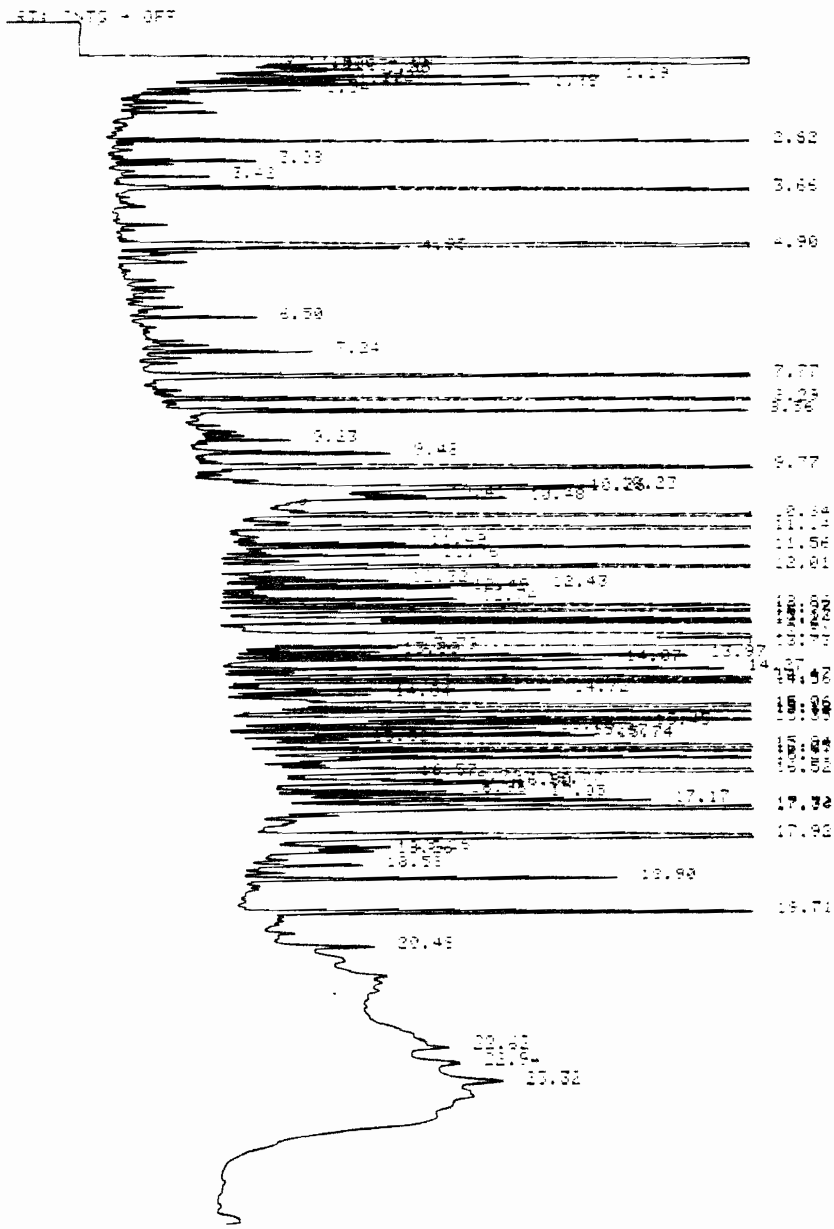

Figure 2 Chromatogram of Basic Extract from a Case Sample

Indeed, without obvious visual contamination, the only drugs of potential significance are the "caines", for example, cocaine and other local anaesthetics such as lidocaine and tetracaine (which are used as cocaine adulterants). The free bases or hydrochloric acid salts (most commonly encountered in "street" samples) would be extracted by this method as both forms are extremely soluble in ethanol. The physical packaging of other drugs, that is, in capsule or tablet form would tend to preclude their transfer to currency with the exception of nicotine which is invariably present on old currency as a result of being handled by smokers.

The second question concerns the need for a blank or drug free currency sample for casework comparison. The only true blank would be new, untouched currency. Extraction of cocaine from this currency would not be realistic because of the lack of normal components which certainly affect recoveries (described later with the selection of an internal standard). A true blank is not essential but a sample of currency which is representative of background levels found on notes in general circulation is critical in a comparative study of this type.

Background Currency Samples

In order to compare background levels of representative currency samples to case samples, there are a number of considerations. The sample must be truly representative of the geographical area where the offence occurred. The samples for background determinations should have been in circulation for a reasonable period of time and one should be able to estimate that time period. The background samples should be analyzed over the average lifetime of the denominations to which they are compared; preferably the analysis should occur as close as possible to the time of the offence. A background sample should be run at the same time as the case sample is analyzed to provide assurance that there have not been drastic changes in the maximum level of these background determinations.

In this work, there were four individual studies on background currency samples. Each sample consisted of 100 notes of each denomination up to and including one hundred dollar notes. Samples were obtained from and extracted in the Bank of Canada, at Regina, Saskatchewan between January and August of 1988.

Currency Flow

Currency flow or distribution in Saskatchewan is shown in Figure 3. All currency used at the chartered banks, credit unions and trust companies, originates ultimately from the Bank of Canada at Regina, Saskatchewan. This currency is processed by a "currency verification, counting, and sorting" machine (developed by R.E.I. Ltd. of Dallas, Texas, USA). This machine also automatically processes (verification of denomination) and shreds notes that are too worn to be distributed again. Table 1 shows the amount of currency destroyed in 1987. Currency which cannot be automatically verified for shredding because it is inordinately worn or torn, possible counterfeits, or two or more notes stuck together, is rejected and examined manually. It was from this group that samples were obtained. Average lifetimes of this currency are shown in Table II. For example, analysis of batches of five dollar notes is indicative of background levels accumulated during the average lifetime of one year in general circulation.

Recovery Study

Contamination of currency which is consistent with being related to cocaine use or trafficking is more likely to be on the surface of currency rather than well absorbed into the paper (1). The analytical scheme used in this work was designed to take this into account.

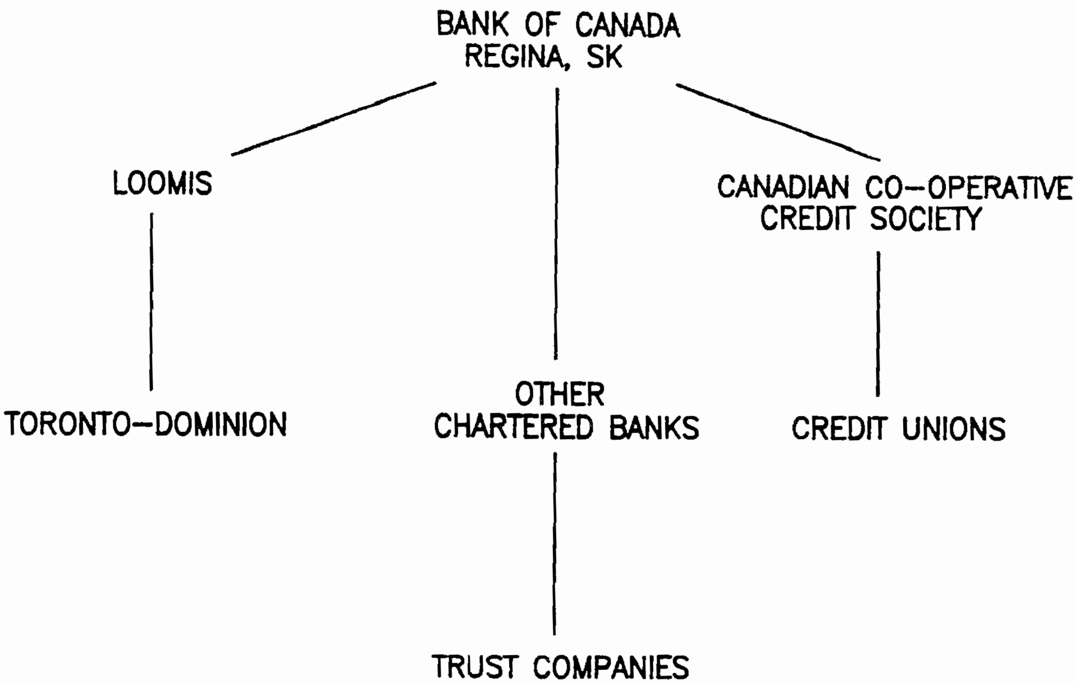

Figure 3 Currency Flow in Saskatchewan

TABLE I

DESTRUCTION OF CURRENCY IN SASKATCHEWAN (1987)[2]

Denomination	Total (Notes)
1	15,336,700
2	839,800
5	5,651,400
10	3,065,300
20	7,074,600
50	495,000
100	257,900
1000	249

[2]Personal Communication, G. Page, Agent, Bank of Canada, June 23, 1988.

TABLE II

AVERAGE LIFETIME OF BANKNOTES[3]

Denomination	Years
1	1
2	1
5	1
10	1.5
20	2.5
50	4.5
100	8.5

[3]From a Statement made by John Crow to the House of Commons Standing Committee on Miscellaneous Estimates April 15, 1985, Personal Communication, G. Page, Agent, Bank of Canada, June 23, 1988.

Each piece of currency was immersed in ethanol for a short period of time in order to more selectively extract the surface contaminants.

A recovery study was performed by washing one-dollar bills, ten in total, three times sequentially in ethanol, to remove contaminants. The notes were immersed for 10 minutes in each ethanol wash. The first and second extracts were discarded. The third ethanol extract was analyzed for cocaine using the procedure described in this work and used as a blank (Figure 4). The notes were dryed for at least 30 minutes. Ten microlitres of cocaine standard (at 10 nanograms per microlitre of ethanol) were then streaked across each note with a ten microlitre syringe, and allowed to dry for 30 minutes. Each of the 10 spiked notes was dipped sequentially and the ethanol extract was analyzed (Figure 5) and compared to an injection of 50 nanograms of unextracted cocaine standard (equivalent to 1/20th of

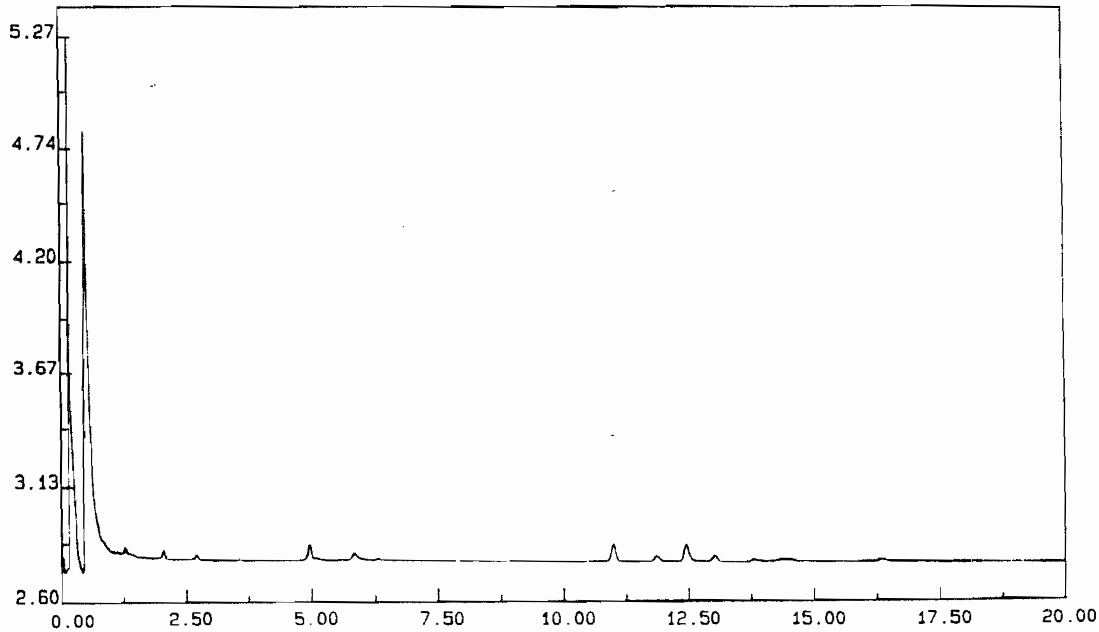

Figure 4 Chromatogram of Ethanol Extract of Currency — Blank

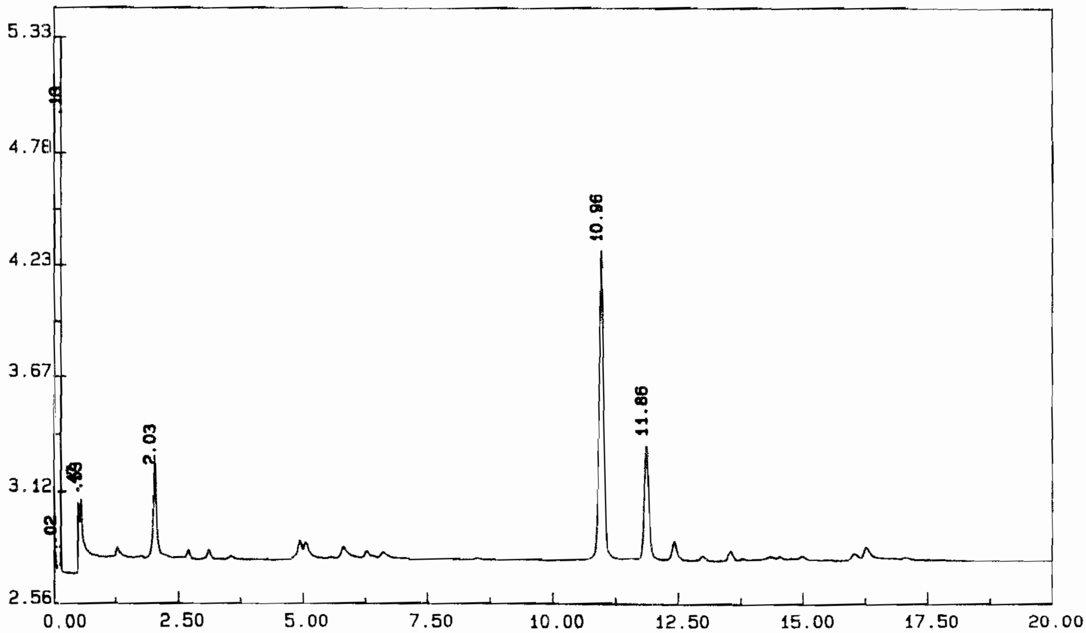

Figure 5 Chromatogram of Cocaine (10.96) Spike of 1's

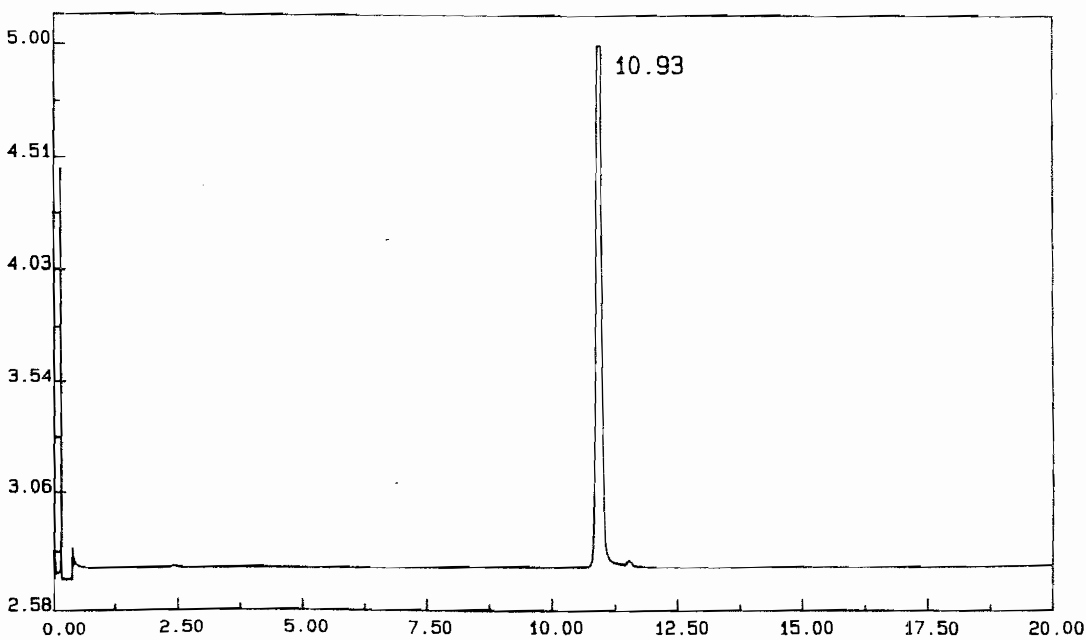

Figure 6 Chromatogram of Unextracted Cocaine (50 ng)

100% recovery) (Figure 6). Overall recovery was 35.6%. Nitrogen-phosphorus detector response to cocaine standards as described above was assessed and found to be linear (R = 0.992) over the 25-1000 nanogram range.

Chloroform-aqueous extraction recovery was also determined by adding a known amount of cocaine (1000 nanograms) to ten millilitres of chloroform, performing the procedure as above, then comparing again to an unextracted cocaine standard (1/20th of the residue from the chloroform extract compared to an injection of 50 nanograms of cocaine). Recovery from chloroform was 72.9%. This indicates significant losses in the ethanol evaporation stage and/or dissolving the remaining residue into chloroform compared to the organic-aqueous extraction procedure.

Currency Studies

Four individual background currency samples were analyzed quantitatively and the results are summarized in Table III.

Study 1

The first study was performed to determine the extent of cocaine contamination on currency in general circulation in Saskatchewan. A gas chromatograph (HP5880A) equipped with a nitrogen-phosphorus detector, a 100:1 split injector, and operated under conditions described above was used to check for gross contamination, that is, samples containing microgram quantities of cocaine per denomination. Figure 7 shows an injection of 1/20th of the extract from the ten dollar notes. Background cocaine levels were not readily detected at this sensitivity. The minimum detectable amount of cocaine at the detector was 0.5 nanogram (i.e. 1000 nanograms of cocaine must be present in the extract for 1/20th (50 ng), split 100:1 to be detected). The same injection, shown in Figure 8, is a splitless injection at more than 100 times the sensitivity. In this study (and studies 2 and 3) the amount of cocaine per note was determined by comparison to integration counts per nanogram of cocaine calculated from the nearest standard added to chloroform and run through the above procedure. These values are mean amounts of cocaine per note.

Except where indicated in Table III, each batch of 100 notes per denomination analyzed, contained less than 1 nanogram of cocaine per note.

TABLE III

COCAINE QUANTITATION OF BACKGROUND CURRENCY
(Average per banknote in nanograms)

Denomination	Study 1	Study 2	Study 3	Study 4(+)
1	0.30	—++	—	2.41 (7.38)
2	0.25	—	—	1.56 (5.83)
5	0.13	—	0.53	N/D (34.3)*
10	0.49	—	—	69.4 (362)*
20	0.13	15.9*	—	6.84 (1.97)
50	0.24	0.80	0.88	6.06 (1.36)
100	0.27	0.27	1.73	N/D (177)*

+ Some batches in this study appeared particularly worn and dirty compared to studies 1 to 3. (GC/MF quantitations shown in brackets).
++ No detectable cocaine
* Gross contamination (procaine also detected on 20's of Study 2)
N/D Not determined — chromatograms too complex for cocaine determination

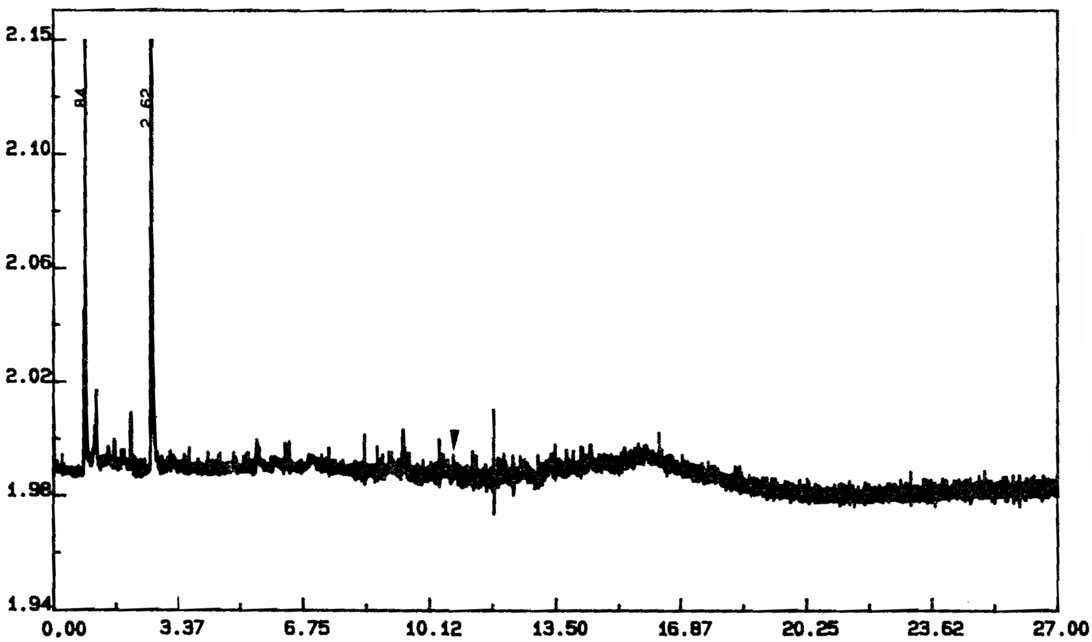

Figure 7 Chromatogram of Extract from 10's — Split 100:1

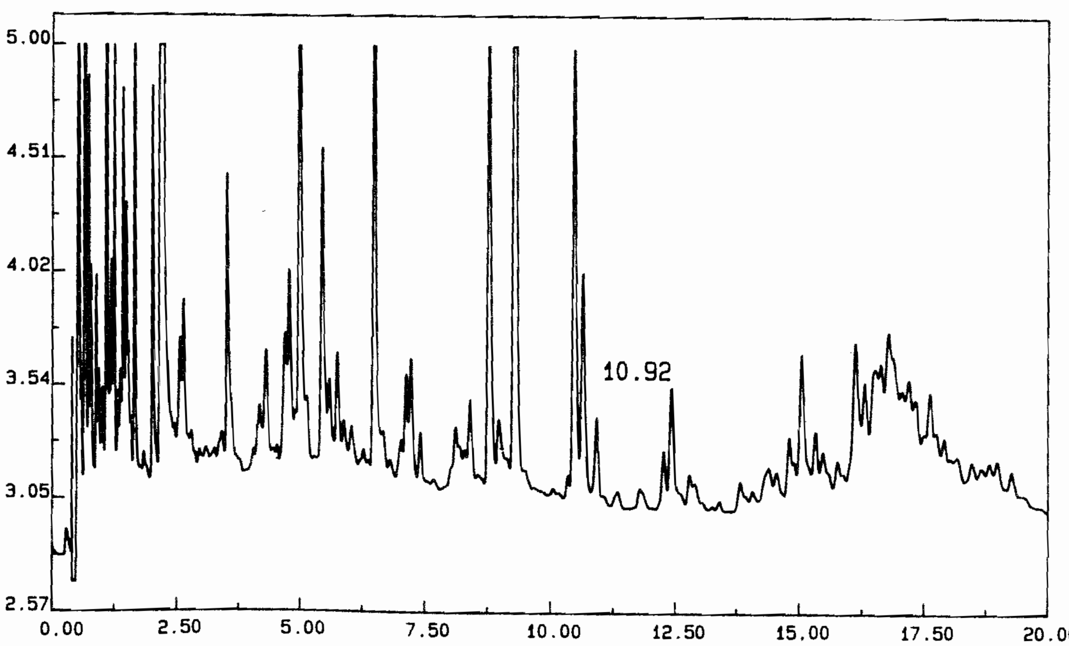

Figure 8 Chromatogram of Extract from 10's — Splitless

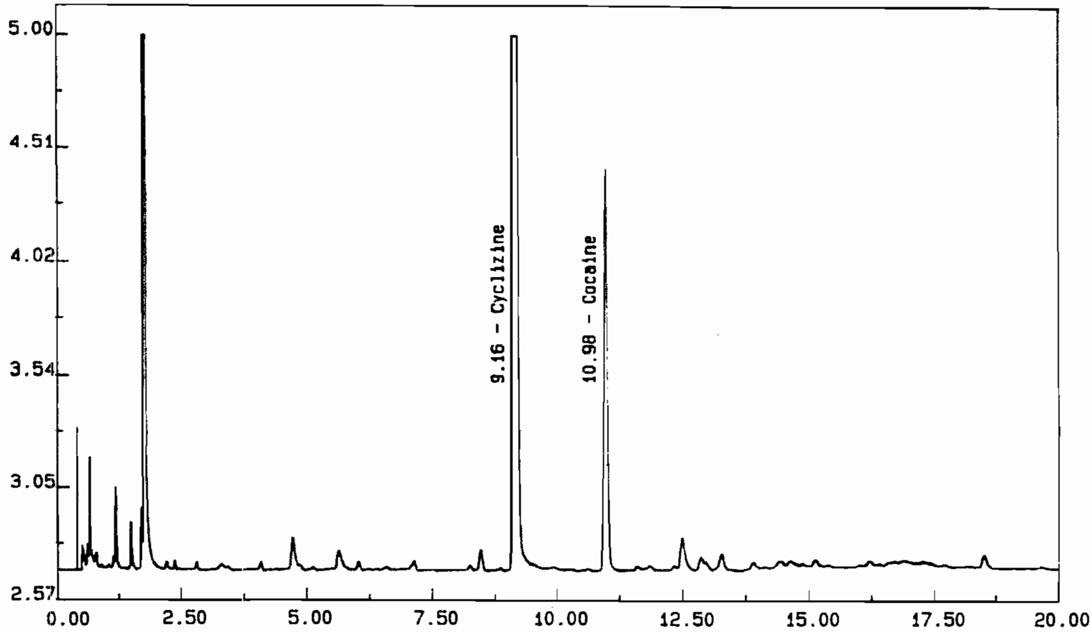

Figure 9 Chromatogram of I.S. (1000 ng) & Cocaine (200)

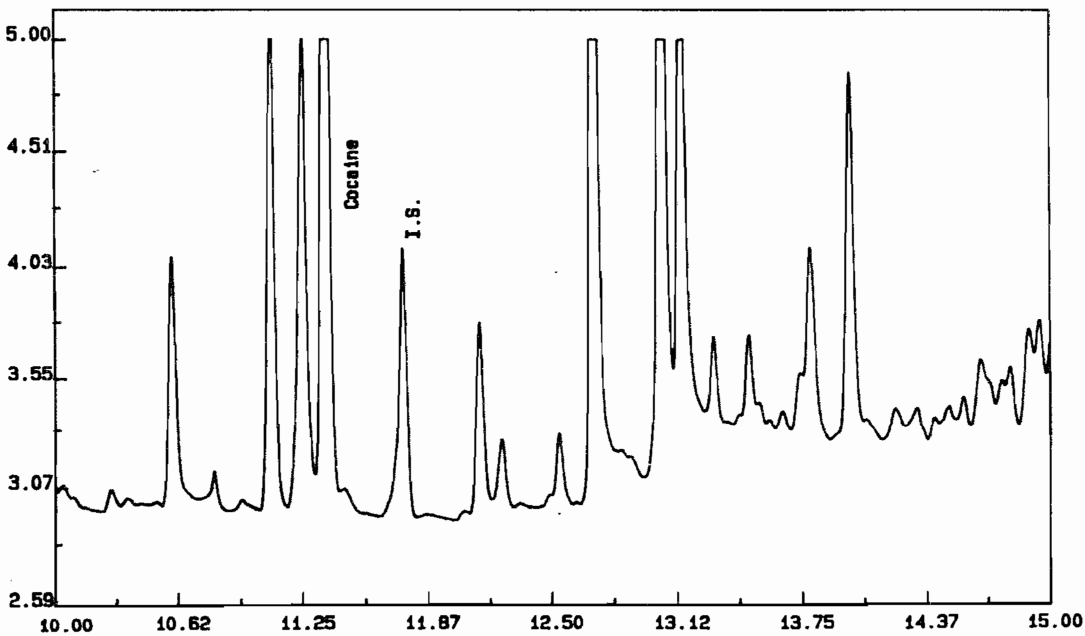

Figure 10 Chromatogram of Study 4 — $5 Notes

Studies 2 and 3

In the next two studies attempts were made to find an appropriate internal standard that was well separated from the normal constituents of the currency extracts. Clomipramine, cyclizine (Figure 9), and desipramine worked well for standard curves prepared by direct addition of the drug to the chloroform. However, these internal standards could not be detected when added to the chloroform solution used to dissolve the residue remaining after evaporation of the ethanol. Quantitative results (Table III) were determined, as for study 1, based on absolute amounts of cocaine, corrected only for chloroform and aqueous extraction losses.

Study 4

This study was done using the "caine-like" internal standard, bupivacaine. Bupivacaine had not been investigated initially because of the remote possibility of encountering it in actual casework. Even though bupivacaine is marketed in Canada and the United States only in injectable form (Marcaine, manufactured by Winthrop), diversion from a legal source is a potential concern. However the presence of bupivacaine would be obvious because of drastic increases in internal standard integrations compared to the standards and other case denominations analyzed.

Bupivacaine was detected in extracts analyzed by GC with NPD (Figure 10), but quantitation was difficult due to the many interfering components. For this reason, the GC

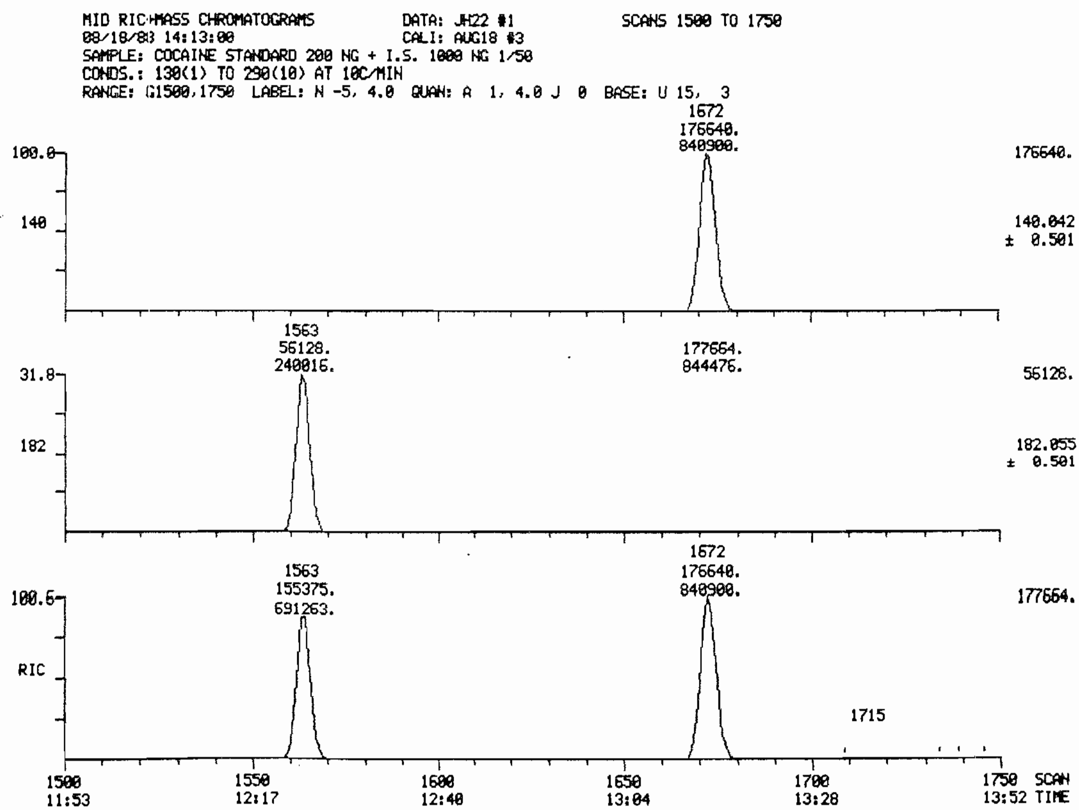

Figure 11 GC/MF Quantitation

FIGURE 12 – GC/MF REGRESSION ANALYSIS

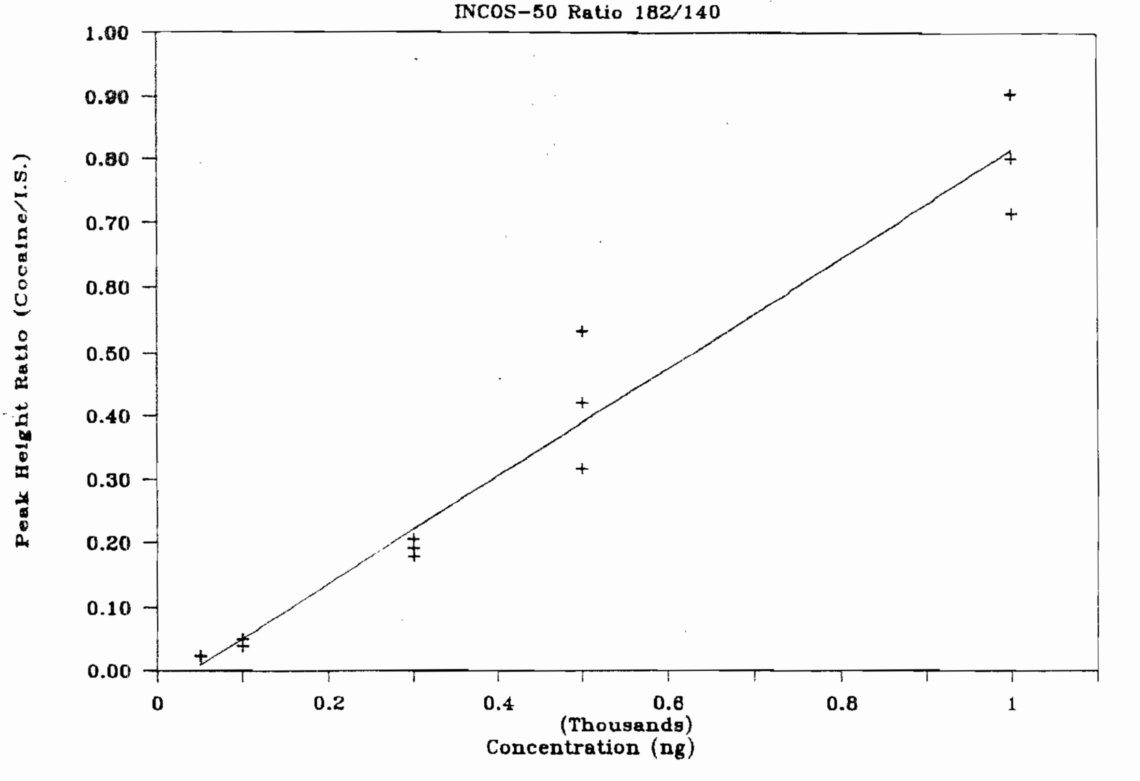

Figure 12 GC/MF Regression Analysis

results reported in Table IV were not corrected using the internal standard and are estimates only. A gas chromatography/mass fragmentography (GC/MF) method was developed to eliminate the interference problems. Selected ion monitoring (SIM) of three ions for cocaine (82,182,303) and two ions for bupivacaine (140,207) was done on the standards and background currency extracts from study 4. Quantitative determinations were done by plotting the ratio of 182 ion to 140 ion peak heights (Figure 11) versus cocaine concentration (Figure 12) from 25 to 1000 nanograms per sample. A total ion chromatogram for a typical currency extract is illustrated in Figure 13.

In future studies selected ion monitoring will be limited to two ions: 182 for cocaine and 140 for the internal standard. Monitoring just the two ions will increase integration time, hence sensitivity, and eliminate the effects of baseline rise from the 207 ion, which is a common ion for methyl silicone (DB-1 column bleed).

Application to Case Samples

To this date, five separate currency samples have been analyzed: four submitted as a result of drug investigations, and one under Section 312 of the Criminal Code. The case sample results are summarized in Table IV. The quantitative results in nanograms per note were determined by the GC method only using absolute amounts and are not corrected via the use of an internal standard. Future studies will employ the GC/MF method. Comparing the background levels from studies 1, 2, and 3, in which the maximum cocaine levels are generally less than one nanogram per note, it is obvious that case samples exhibit gross contamination by cocaine. Depending upon the number of notes from each

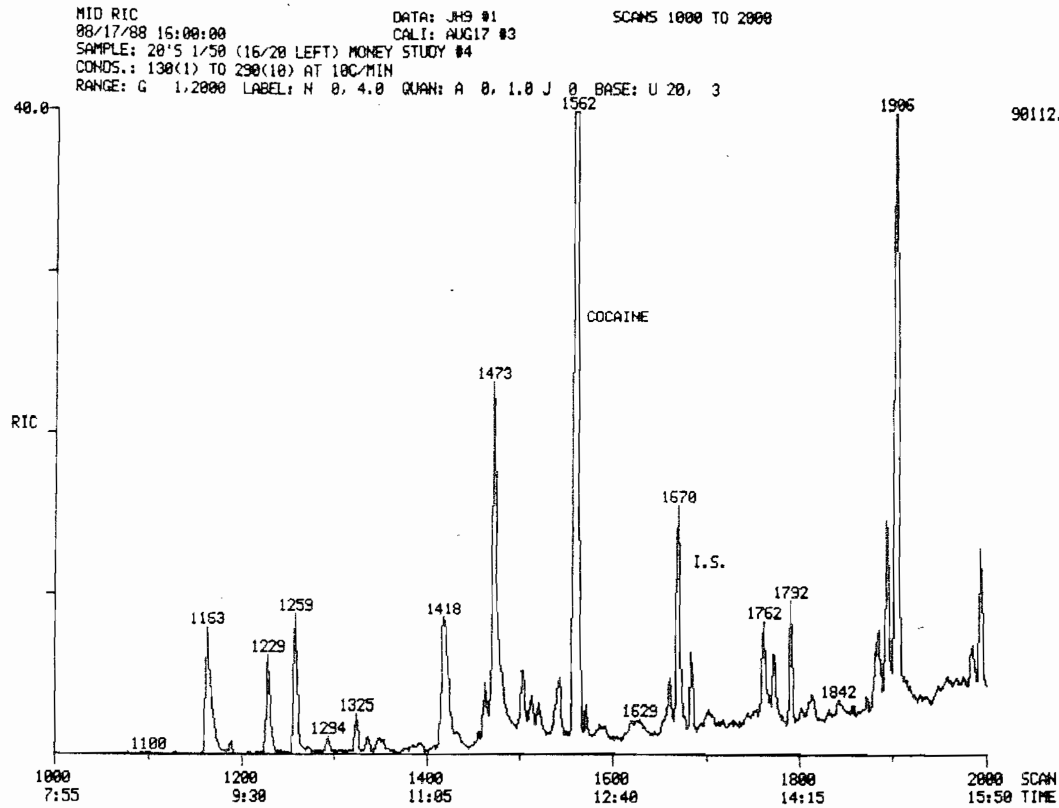

Figure 13 Total Ion Chromatogram of GC/MF Currency Extract

TABLE IV

COCAINE QUANTITATION OF SEIZED CURRENCY
(Average per banknote in nanograms)

Note	A (3999)+	B (3890)	C (842)	D (525)	E (500)
1	−++(14)*	—	— (2)	—	—
2	—	—	—	—	—
5	2.7**(25)	2915 (2)	—	52.7(1)	—
10	314**(14)	14.4(16)	14 (12)	1069(4)	—
20	6.2 (21)	6.2 (26)	5.6(36)	11 (14)	9.2(15)
50	72.8 (6)	115 (38)	—	759 (4)	35.1(4)
100	57.4 (30)	48 (13)	—	—	—

+ Total value of seized currency sample A
++ No detectable cocaine
* Number of notes in each denomination
** Lidocaine and tetracaine were detected on 5's and 10's.

denomination and the number of denominations contaminated, the results for these case samples, which are greater than 50 times the background level, should be regarded as significant. This gross cocaine contamination is consistent with cocaine involvement (be it use or trafficking) and can be considered distinct from the results obtained on currency from general circulation in this province.

ACKNOWLEDGMENTS

The author would like to thank Mr. Graham Page, Agent, Bank of Canada, Regina, Saskatchewan and his staff for their kind assistance and co-operation in the mechanics of the project and in reviewing the manuscript.

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Attachment C3

Oyler, J., Darwin, W.D., and Cone, E.J., Cocaine Contamination of United States Paper Currency, *J. Analyical Toxicology*, **20:**4: 213-216 (1996).

Cocaine Contamination of United States Paper Currency

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Abstract

The exchange of illicit cocaine for money by drug dealers is an everyday occurrence in cities in the United States. There is ample opportunity during the exchange, storage, and use of cocaine for paper currency to become contaminated. Because currency is exchanged frequently, it is likely that contaminated currency would be found in common use. We examined ten single dollar bills from several cities in the United States for the presence of cocaine. Individual bills were extracted with methanol (10 mL). Cocaine was purified from the methanol extract by solid-phase extraction (SPE). The SPE extract was analyzed by gas chromatography–mass spectrometry (GC–MS). Standard curves were constructed with new, uncirculated currency. Cocaine was identified qualitatively by full scan and quantitated by selected ion monitoring. Cocaine was present in 79% of the currency samples analyzed in amounts above 0.1 µg and in 54% of the currency in amounts above 1.0 µg. Contamination was widespread and was found in currency from all sites examined. Cocaine amounts were highly variable and ranged from nanogram to milligram amounts. The highest amount of cocaine detected on a single one-dollar bill was 1327 µg. These results indicated that cocaine contamination of currency is widespread throughout the United States and is likely to be primarily a result of cross-contamination from other contaminated currency and from contaminated money-counting machines.

Introduction

Estimates of illicit cocaine available for consumption in the United States during 1993 range from 243 to 340 metric tons (1). The packaging, distribution, sale, and use of this immense drug supply by dealers and users undoubtedly causes local environmental contamination. Articles of clothing, personal belongings, households, and even public areas are likely to become contaminated from contact with the drug. Concern has been expressed that casual contact with contaminated items might transfer cocaine to the hands of uninvolved individuals. ElSohly (2) evaluated whether individuals who handled cocaine contaminated money would test positive by urinalysis. Two one-dollar bills were immersed in dry, powdered cocaine, and then shaken free of loose cocaine. One individual then handled the money several times during the course of the day. Analysis of urine samples collected over a period of approximately 24 h after handling the contaminated money revealed that the individual excreted a maximum of 72 ng/mL of benzoylecgonine 12.5 h after handling had occurred. It was concluded that casual handling of articles contaminated with cocaine would not result in a positive urine test at a cutoff concentration of 300 ng/mL of benzoylecgonine.

The sale of illicit cocaine is often associated with the exchange of large sums of money, which may become contaminated. Indeed, the presence of cocaine on money is often interpreted as evidence of drug trafficking and is used in court proceedings (3). Cocaine contamination of paper currency is believed to be widespread based on anecdotal reports, but only a few studies have documented the presence of cocaine on money (3,4). We examined circulated paper currency ($1 denominations) collected from 14 cities in the United States for the presence of cocaine and related analytes in an attempt to determine the extent of contamination.

Materials and methods

Chemicals, reagents, and materials

Cocaine hydrochloride was obtained from Mallinckrodt, Inc. (St. Louis, MO). Benzoylecgonine tetrahydrate, norcocaine, and ecgonine methyl ester hydrochloride were obtained from the National Institute on Drug Abuse (Rockville, MD). Cocaethylene and norcocaethylene fumarate were obtained from Research Triangle Institute (Research Triangle Park, NC). Anhydroecgonine methyl ester oxalate and ecgonine ethyl ester were obtained from the Addiction Research Center, National Institute on Drug Abuse (Baltimore, MD). Deuterated analogues of cocaine, benzoylecgonine, cocaethylene, and ecgonine methyl ester were obtained from Sigma Chemical Co. (St. Louis, MO).

N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) with 1% trimethylchlorosilane (TMCS) was obtained from Pierce

Chemical Co. (Rockford, IL). All organic solvents were HPLC grade and chemicals were reagent grade. Acetate buffer (pH 4.0 ± 0.1) was prepared with 2.0M sodium acetate and 2.0M acetic acid. The elution solvent, methylene chloride–isopropanol–concentrated aqueous ammonium hydroxide (80:20:2, v/v/v), was prepared daily. Extraction columns, CLEAN SCREEN® (ZCDAU020), and the vacuum manifold system (VMF024GL) were purchased from United Chemical Technologies (Bristol, PA).

Instrumentation

Analyses were performed on a Hewlett-Packard (Wilmington, DE) 5890A gas chromatograph with an autosampler (HP7673A) interfaced with a Hewlett-Packard 5970B mass selective detector (MSD). A split–splitless capillary inlet system and a HP-1 fused-silica capillary column (12 m × 0.2-mm i.d., 0.33-µm film thickness) were used for cocaine analyses.

Collection of United States paper currency

Paper currency ($1 denominations) was collected in 14 cities in the United States and was in general circulation at the time of collection. The money was placed in plastic freezer bags and shipped to the Addiction Research Center for analysis. Uncirculated and uncut currency was purchased from the United States Treasury Department, Washington, D.C., for use as drug-free control currency.

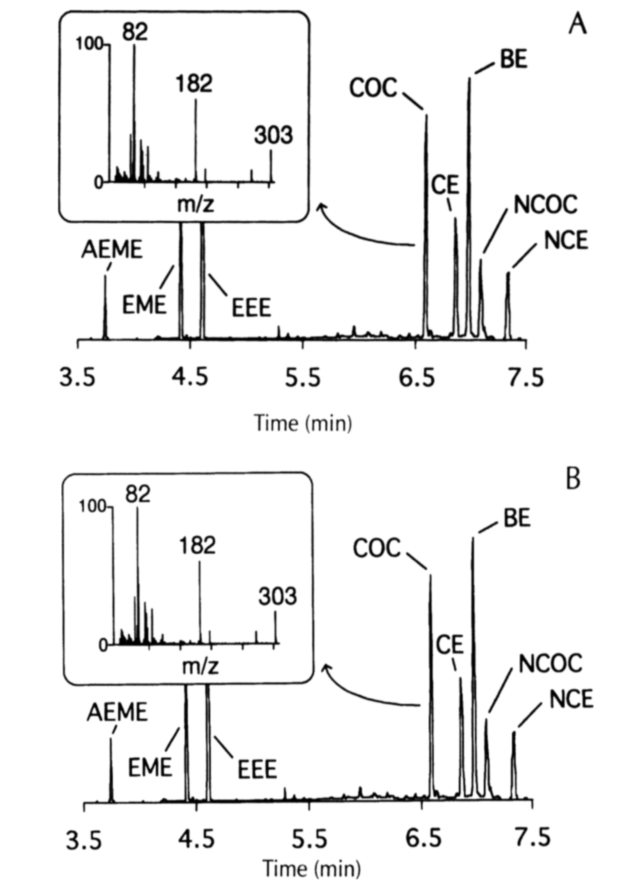

Figure 1. Total ion current recordings of extracts from uncirculated currency with added cocaine standards (A) and circulated United States currency ($1 denomination from Spanish Fort, AL) (B). Insets represent the mass spectrum of cocaine obtained in each run. Cocaine content in the Spanish Fort, AL currency was 70.2 µg/bill and benzoylecgonine was 3.6 µg/bill. Cocaine standards were added to uncirculated currency in amounts from 250-500 ng. Analytes are identified as follows: AEME = anhydroecgonine methyl ester; EME = ecgonine methyl ester; EEE = ecgonine ethyl ester; COC = cocaine; CE = cocaethylene; BE = benzoylecgonine; NCOC = norcocaine; NCE = norcocaethylene.

Extraction and analysis of currency

Single currency bills were placed in 15-mL centrifuge tubes and extracted with 10 mL methanol. The tubes were capped, agitated for 2 min, and allowed to stand at room temperature for 1 h. Aliquots (1-mL) were removed and treated with deuterated internal standards (500 ng each). Samples were extracted by solid-phase extraction (SPE) followed by gas chromatography–mass spectrometry (GC–MS) over analysis according to a published procedure (5). Briefly, the procedure consisted of addition of sodium acetate buffer (3 mL, 2M, pH 4.0) to each sample, followed by mixing. Samples were filtered through 4-mL fritted filters, and the eluent was decanted onto preconditioned SPE columns. The columns were washed with deionized water (1 × 2 mL) and 0.1 M HCl (1 × 1.5 mL) and aspirated to dryness for 2 min. Methanol was added (2 × 1 mL) and the cartridges were again aspirated to dryness for 2 m. The analytes were eluted into clean tubes with elution solvent (6 × 1 mL). Extracts were evaporated to dryness at ambient temperature under nitrogen and reconstituted in 20 µL acetonitrile. The samples were transferred to autosampler vials (0.1-mL) and derivatizing reagent (20 µL BSTFA with 1% TMCS) was added. The vials were sealed and heated at 60°C for 30 min. One microliter was injected for GC–MS analysis. The samples were analyzed in the scan mode for identification purposes and in the selected ion monitoring mode for quantitation. Cocaine was measured in currency extracts by internal standardization and comparison of responses to standard curves constructed with unused, drug-free currency. Standard curves were run in duplicate with each batch of currency and contained cocaine, ecgonine methyl ester, and benzoylecgonine in amounts of 0, 12.5, 25, 50, 100, 250, and 500 ng and anhydroecgonine methyl ester, ecgonine ethyl ester, cocaethylene, norcocaine, and norcocaethylene in amounts of 0, 6.25, 12.5, 25, 50, 125, and 250 ng. Duplicate control samples were also analyzed with each batch. Control samples were prepared with drug-free currency and contained cocaine and benzoylecgonine at two amounts (100 ng and 500 ng per extract).

Results

Cocaine was extracted from currency bills and identified by GC–MS operating in the full scan mode. Additional derivatives and metabolites of cocaine were included in the analysis to determine if they were also present on money. Figure 1A illustrates the response of cocaine analogues (500 ng/250 ng) extracted from a single uncirculated currency bill (without internal standard). The inset contains the mass spectrum of standard cocaine at a retention time of 6.6 min that was obtained in the same run. Figure 1B illustrates the response from an extract of a single piece of circulated currency collected in Spanish Fort, AL.

Cocaine was identified by comparison of the mass spectrum of the peak with a retention time of 6.6 min (see inset) with that of the cocaine standard. The characteristic ions of cocaine at *m/z* 303, 182, and 82 provided unequivocal evidence of the identity of cocaine in this currency. The currency extract (Figure 1B) also contained traces of benzoylecgonine (retention time, 7.1 min) that was identified by mass spectral comparison. Quantitative analysis of the Spanish Fort, AL, currency illustrated in Figure 1 provided an estimate of the total amount of cocaine and benzoylecgonine present. There was a total of 70.2 µg cocaine and 3.6 µg benzoylecgonine present in the single piece of currency. Benzoylecgonine was identified in 17% (N = 136) of the currency bills analyzed. No other cocaine constituents were detected in the analyses.

Quantitation of cocaine and benzoylecgonine in individual bills was accomplished by GC–MS operating in the selected ion monitoring mode. Currency extracts were treated with deuterated internal standards (500 ng) and extracted by SPE, derivatized and analyzed together with calibration standards and control samples that contained known amounts of cocaine analytes. Calibration curves were linear across the range from 0 to 500 ng of cocaine extracted from unused currency. Correlation coefficients were typically greater than 0.99. Between-run coefficients of variation were less than 5% for control samples containing 100 and 500 ng of cocaine. The limit of quantitation was arbitrarily selected as 12.5 ng, the lowest point on the calibration curve. Recovery of cocaine from currency was evaluated by extracting currency that had been previously extracted. A mean amount of 20.5 µg of cocaine was present in the first extract (N = 5 individual pieces of currency) and a mean amount of 2.3 µg was present in the second extract. Correction for the residual cocaine left by the first extraction solvent (1 mL of the first solvent was retained by the paper currency) indicated that greater than 95% of cocaine present was removed in the first extract. Analysis of all extracts of uncirculated currency were negative for cocaine and analytes.

Table I. Cocaine concentrations in United States Paper Currency ($1 denominations) from Selected Cities

City	Number positive (>0.1 µg/bill)	Number positive (>1.0 µg/bill)	Mean amount (µg/bill)	Range (µg/bill)
Baltimore, MD	9	9	75.7	0–597.0
Miami, FL	3*	2*	2.5	0–13.1
Chicago, IL	7	4	0.7	0–2.2
Honolulu, HI	10	5	3.0	0.2–9.9
Kansas City, KS	9	8	6.3	0–24.3
Las Vegas, NV	9	5	3.9	0–13.9
Los Angeles, CA	9	6	3.9	0–11.4
Minneapolis, MN	8	6	63.8	0–559.8
Spanish Fort, AL	9	7	9.0	0–70.3
Ft. Wayne, IN	9	6	3.8	0–16.6
Pittsburgh, PA	4	1	0.4	0–2.6
Yellowstone, WY	5	2	1.9	0–14.5
Whitefish, MT	7	4	0.9	0–3.0
Portsmouth, OH	10	9	136.9	0.5–1327.0

* N = 10 for all collection points except Miami, FL, where N = 6

Cocaine was present in 79% of the currency bills in amounts above 0.1 µg and in 54% of the currency bills in amounts above 1.0 µg. Contamination was widespread and was found in currency from all collection sites. Cocaine amounts were highly variable and ranged from nanogram to milligram amounts (Table I). The highest amount was 1327 µg found on a single bill from Portsmouth, OH. This bill also contained the highest amount of benzoylecgonine (146.6 µg). Generally, benzoylecgonine was present in amounts not exceeding one-tenth that measured for cocaine.

Discussion

This study demonstrated that $1 denominations of circulated United States paper currency are highly contaminated with cocaine. With the exception of benzoylecgonine, a hydrolysis product of cocaine, other derivativates of cocaine were not present. The absence of anhydroecgonine methyl ester would seem to indicate that "crack" cocaine vapor was not the source of contamination because this pyrolysis product is produced when cocaine is smoked (6). Cocaine was detected in individual bills from all collection sites. No obvious trend in amount or frequency of contamination was observed for different geographical areas. Currency from less populous areas (e.g., Whitefish, MT and Yellowstone, WY) tended to have lower amounts, but highly populous areas like Chicago, IL, also had low cocaine content compared with some areas. The small number of bills collected at each site and the nonrandom method of collection precluded generalizations regarding geographical area.

The cause of the widespread cocaine contamination of paper currency ($1 denominations) is unclear. It seems highly unlikely that the majority of all one-dollar bills in circulation have been involved in illicit drug sales and drug exchanges. It is possible that currency becomes contaminated from contact with previously contaminated currency and with money counting machines in financial institutions. If this is the case, contamination would begin as soon as uncirculated currency is introduced into circulation. Contamination could even occur during handling and processing prior to general circulation. The average lifespan of a one-dollar bill in the United States is approximately 12 months. During this period, many exchanges between individuals and financial institutions occur. These exchanges would provide ample opportunity for cross contamination from other currency.

The results from this study suggest that the presence of cocaine in amounts up to 1 mg per bill does not signify that the currency was involved in a drug transaction. Once contaminated, currency is likely to remain contaminated during the remainder of its circulation. Cocaine binding studies with tritium-labeled cocaine in our laboratory have shown that the paper matrix of one-

dollar bills has the capacity to bind cocaine in a specific, reversible manner not unlike biological binding sites (unreported data). The high binding affinity and capacity of United States paper currency for cocaine may explain why cocaine is retained on currency. Although the ubiquity of cocaine on money lessens its value as a marker for illegal drug transactions, other tests for cocaine may be performed.

Aaron and Lewis (4) suggested an alternate test could be performed by law enforcement to determine if specific bills were used in cocaine transactions. They placed circulated currency inside polyester envelopes and shook them to remove loose cocaine powder. The interior of the envelope was washed with methanol and analyzed by GC–MS. The presence of cocaine in the envelope was considered corroborative evidence that the money had been involved in the sale or use of cocaine. They also tested normal, circulated currency in denominations of $10 to $100. No cocaine was found in the methanol washes of the envelopes following shaking; consequently, it was suggested that the test would distinguish "drug transaction" currency from normal, circulated currency. It is noteworthy, however, that further analysis of methanol washes of the normal, circulated currency also revealed the presence of cocaine. As a result of that study and findings from the current experiments, it can be concluded that cocaine is present as a contaminant in a majority of all circulated United States paper currency.

Acknowledgments

The authors would like to thank Lee Hearn for helpful discussions regarding the analysis of cocaine on currency and Robert E. Joseph, Jr. for data on cocaine binding to currency.

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Manuscript received August 23, 1995;
revision received December 1, 1995.

Attachment C4

Negrusz, A., Perry, J.L., and Moore C.M., Detection of Cocaine on various Denominations of United States Currency, *J. Forens. Sci.*, **43**:3 (1998).

TECHNICAL NOTE

Adam Negrusz,[1] Ph.D.; Jennifer L. Perry,[1] B.S.; and Christine M. Moore,[2] Ph.D.

Detection of Cocaine on Various Denominations of United States Currency

REFERENCE: Negrusz A, Perry JL, Moore CM. Detection of cocaine on various denominations of United States currency. J Forensic Sci 1998;43(3)626–629.

ABSTRACT: The presence of cocaine on U.S. paper currency collected in many cities in the United States has previously been reported. Currency becomes contaminated during the exchange, storage and use of cocaine. Different currency denominations are also rolled by drug users and used to snort cocaine. Illicit cocaine is widely abused and therefore the contaminated paper currency can be easily found in common use. A total of 18 bills were analyzed in our laboratory for cocaine. Ten $20 bills were randomly collected in Rockford, IL and four $1 bills in Chicago. An additional four uncirculated $1 bills were analyzed as a control group. All bills were extracted with 0.1 M hydrochloric acid followed by solid-phase extraction. Cocaine was identified using gas chromatography/mass spectrometry in full scan mode, and drug quantitation was performed in selected ion monitoring mode. A standard curve was prepared and doxepin was used as an internal standard. In addition, for method validation two levels of control solutions were analyzed simultaneously. Precision and accuracy values were within acceptable ranges. Cocaine was present on 92.8% of all bills collected from the general circulation. All $20 bills were contaminated with cocaine and the amount of drug varied from 0.14 to 10.02 μg of cocaine per bill ($\bar{x}$ = 2.86 μg). Only one $1 bill was cocaine free. In one case ($1 bill), only traces (below quantitation limit) of cocaine were found. All four uncirculated $1 bills were cocaine-free.

KEYWORDS: forensic science, drugs of abuse, contamination of currency, cocaine, solid-phase extraction, gas chromatography-mass spectrometry

United States paper currency has been reported to be contaminated with illicit cocaine due to the enormous extent of cocaine distribution, sale and consumption. Previously cocaine was found on paper currency collected in 14 different size cities in the United States (1). At present and based on the existing analytical data it is accurate to say that the paper currency contamination of cocaine is widespread. In fact, most Americans handle small amounts of cocaine every day, not as packets sold by drug dealers, but on the dollar bills that line their pockets. Considering all this information, can casual contact with money contaminated with cocaine result in positive urinalysis? In one study (2), the reported concentration of benzoylecgonine in urine following casual contact with cocaine-contaminated currency was below the cutoff value of 150 ng/mL for this particular cocaine metabolite. It has also been suggested that currency becomes contaminated from contact with previously contaminated bills in financial institutions. There are sometimes even hundreds of micrograms (in one case even 1327 μg) of cocaine present on a single bill (1). Widespread currency contamination may cause a problem for people who on a daily basis deal with large numbers of bills: bank tellers, people who operate money counting machines, among others.

The aim of this study was to identify and quantitate cocaine on ten $20 bills collected randomly from the general circulation in Rockford, IL. In addition, four $1 bills were collected randomly in Chicago and analyzed. As a control group, four new and uncirculated $1 denomination bills were analyzed. Gas chromatography/mass spectrometry (GC-MS) was employed for identification and quantitation of drug on paper currency. This study was prompted by the Channel 17 WTVO TV Station in Rockford, which also provided the $20 bills.

Materials and Methods

Drug Standards, Chemicals, and Materials

Cocaine hydrochloride was obtained from Mallinckrodt, Inc. (St. Louis, MO). Doxepin was purchased from Radian International (Austin, TX). Acetic acid glacial was obtained from Sigma Chemical Company (St. Louis, MO). Methylene chloride, hydrochloric acid, isopropanol, ammonium hydroxide and methanol were purchased from Fisher Scientific (Itasca, IL). All organic solvents were high-performance liquid chromatography (HPLC) or HPLC-GC/MS grade, all other chemicals were American Chemical Society (ACS) grade. The elution solvent, methylene chloride isopropanol:concentrated ammonium hydroxide (78:20:2, v/v/v), was prepared fresh every day. ISOLUTE™ HCX 200 mg, 10 mL extraction columns (International Sorbent Technology) were purchased from Jones Chromatography (Lakewood, CO).

Instrumentation

Analysis was performed using a Hewlett-Packard (Palo Alto, CA) 6890 gas chromatograph with HP 6890 Series injector and

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Received 25 July 1997; and in revised form 23 Sept. 1997; accepted 6 Oct. 1997.

5973 mass selective detector (MSD). Samples (1 μL) were introduced to the system via a split-splitless capillary inlet system in a splitless mode, and an HP-5MS fused-silica capillary column (30 m × 0.25 mm × 0.25 μm) was used. The oven temperature program was: 130°C for 1 min, ramp at 12°C/min to 280°C; 280°C for 1 min. The sample inlet temperature was 270°C. The ion source temperature was kept at 230°C and quadrupole temperature at 150°C. Cocaine was identified by GC-MS operating in the full scan mode (35 to 500 amμ) and quantitation was performed in the selected ion monitoring mode (m/z 82, 182, 303 ions for cocaine and m/z 58 for the internal standard, doxepin) using ion ratios of ±20%. Dwell time for each ion was 50 ms.

Currency Collection

Ten paper bills ($20 denominations) were collected randomly from wallets of ten people in Rockford, and four $1 bills were collected at the University of Illinois at Chicago from general circulation (employees and graduate students). Four uncirculated $1 bills were obtained from the Federal Reserve and shipped for analysis in a plastic bag. Single bills were placed in plastic ziplock bags and delivered to the Department of Pharmaceutics and Pharmacodynamics, University of Illinois at Chicago for analysis.

Extraction Procedure

Single bills were placed in 50-mL plastic tubes and 0.1 M hydrochloric acid (5 mL) was added. All tubes were capped, placed on a rotator, and the bills were extracted for 15 min at 30 rpm. A standard curve was prepared for the following concentrations of cocaine: 50, 100, 200, and 500 ng. Control samples were prepared in duplicate at 75 and 300 ng and the specimens were run in two batches. After extraction, aliquots (0.5 mL) were transferred to glass test tubes and internal standard (300 ng, doxepin) was added to each sample, standard and control solutions. Acetic acid (1.93 M, 1 mL) and deionized water (8 mL) were added to each solution and all samples were further extracted using solid-phase extraction. Extraction columns were placed on the vacuum manifold and conditioned with methanol (3 mL), deionized water (3 mL), and acetic acid (1.93 M, 1 mL). All samples were added to the columns and were slowly drawn through. The columns were dried (2 min) and were washed with deionized water (3 mL), hydrochloric acid (0.1 M, 1 mL), and methanol (3 mL). After the last wash, the columns were dried for 5 min and collection tubes were placed in the manifold rack. Drugs were eluted with a mixture of methylene chloride: isopropanol:concentrated ammonium hydroxide (78:20:2, v/v/v) (3 mL). All samples were then evaporated to dryness under a stream of air, reconstituted in methanol (100 μL), transferred to the autosampler vials and placed on the autosampler.

Results

In this study cocaine was identified on 92.8% of all bills analyzed by GC-MS (Table 1). All the extracts from $20 bills were positive for cocaine and the amount of the drug was between 0.14 and 10.02 μg per bill ($\bar{x} = 2.86$ μg). Four $1 bills were analyzed. One bill was negative for cocaine and traces of cocaine (below quantitation limit) were present on another one ($\bar{x} = 0.83$ μg). All uncirculated $1 bills were negative for cocaine. Table 1 gives the results of analysis of all bills for the presence of cocaine. Cocaine retention time was 11.32 min and the drug was identified by comparison of the mass spectrum (full scan mode) with cocaine standards. Quantitation of cocaine with doxepin as an internal standard was performed using GC-MS working in the selected ion monitoring mode. Doxepin retention time was 11.50 min. The standard curve was linear over the range of cocaine concentrations (50 to 500 ng) and had correlation coefficient, slope and intercept of 0.999, -8.6×10^{-3}, and 8.75, respectively. The wash from the specimens was diluted to produce concentrations of cocaine within the linear range. The limit of quantitation (LOQ) was arbitrarily established to be 50 ng, the lowest cocaine concentration on the standard curve, and the limit of detection (LOD) 1 ng of cocaine per bill using the lowest concentration at which ion ratio criteria were met and signal-to-noise was greater than 5. Two sets of control solutions (75 and 300 ng of cocaine per bill) were analyzed. For the 75 ng controls ($N = 8$), the precision and accuracy values were 3.61% and −4.13%, respectively, for the 300 ng control solutions ($N = 8$), the precision and accuracy were 3.24% and 4.86%, respectively. Figures 1*a* and 1*b* represent typical total ion chromatogram and mass spectrum, respectively, of the extract from $20 bill #4.

TABLE 1—*Amounts of cocaine on $20 and $1 denominations collected randomly from general circulation in two Illinois Cities: Rockford and Chicago.*

Denomination	Bill No.	Amount of Cocaine (μg/bill)
$20	1	4.54
$20	2	2.17
$20	3	3.43
$20	4	5.98
$20	5	1.04
$20	6	10.02
$20	7	0.47
$20	8	0.65
$20	9	0.16
$20	10	0.14
$1	11	2.99
$1	12	0.31
$1	13	N.D.*
$1	14	<0.05

*Not detected.

Discussion

This study demonstrates that paper currency ($20 and $1 denominations) randomly collected from the general circulation in the Illinois area is contaminated with cocaine. In the most recent study Oyler et al. analyzed $1 bills collected from the general circulation in several cities in the United States for the presence of cocaine (1). Cocaine was extracted from bills using methanol followed by solid-phase extraction. The drug was identified using GC-MS in full scan mode and quantitation was achieved in selected ion monitoring mode with deuterated internal standards. In addition, all bills were analyzed for benzoylecgonine, ecgonine methyl ester, cocaethylene, norcocaine, anhydroecgonine methyl ester, and norcocaethylene. Benzoylecgonine, a hydrolysis product of cocaine, was present on 17% of the currency analyzed and its amounts did not exceed one tenth of the measured cocaine concentration. All the currency analyzed was negative for other cocaine constituents. In the Oyler et al. study cocaine was present in 79% of the currency samples analyzed in amounts above 0.1 μg and in 54% of the samples above 1.0 μg. Cocaine contamination was found on currency from all the cities examined.

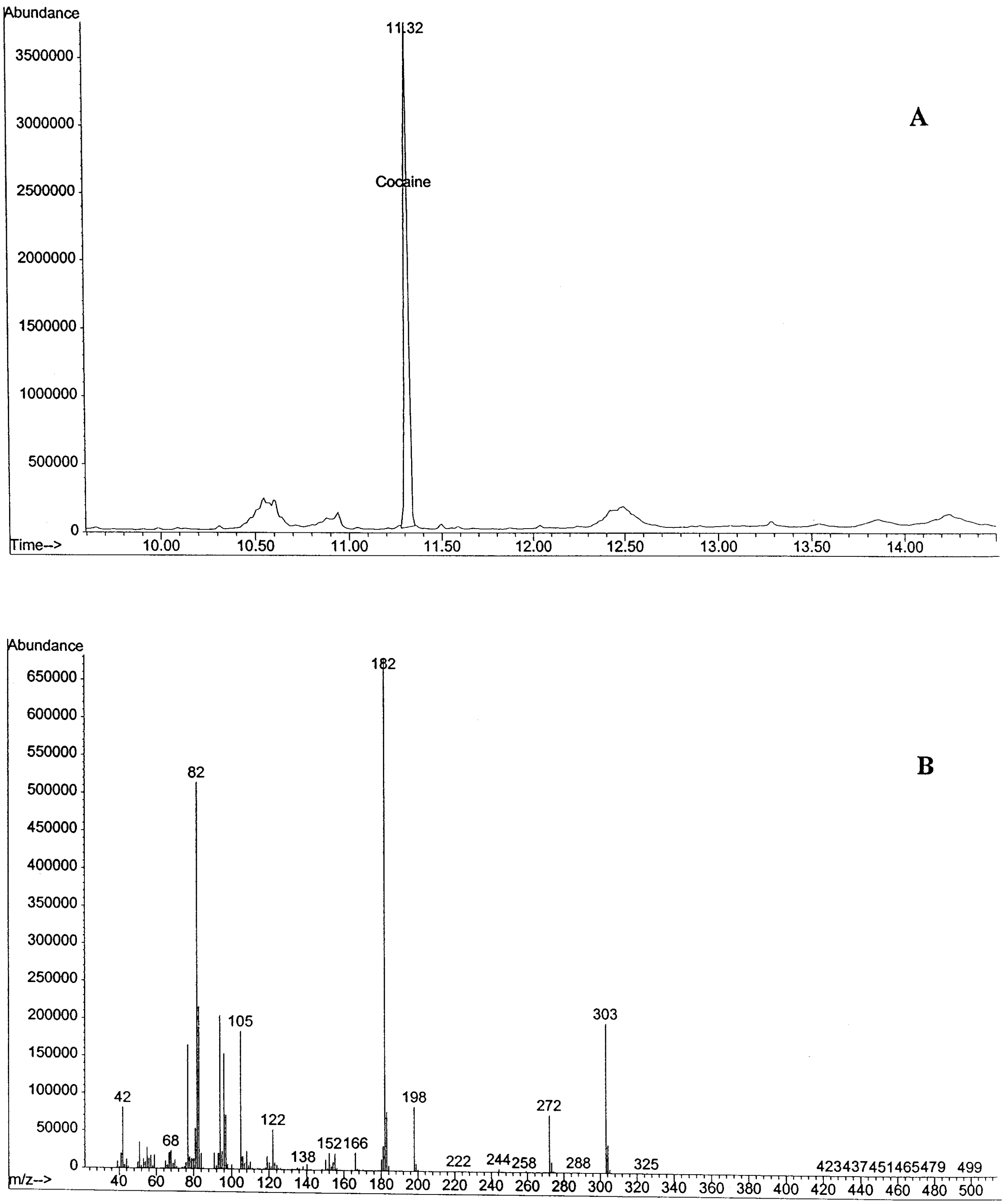

FIG. 1—*Typical total ion chromatogram (A) and mass spectrum (B) of the extract from the twenty-dollar bill #4 (cocaine amount 5.98 μg).*

In this study, the analysis of \$20 bills (10) was carried out for the first time, together with the analysis of four \$1 bills. Cocaine was present on 13 of all bills analyzed (92 8%) and on 12 (85.7%) in amounts above 0.1 μg and on 7 (50%) above 1.0 μg. Ten \$20 bills collected in Rockford, IL were analyzed and they were all positive for cocaine. The results from this study clearly show that \$20 and \$1 denominations circulated in the Illinois area are contaminated with cocaine. In conclusion, based on this study and other data (1) it is accurate to say that the entire population of various denominations of United States currency is contaminated to a significant degree with illicit cocaine.

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Attachment C5

Jenkins, A.J., Drug Contaminations of US Paper Currency, *Forens. Sci. Intnl.*, **121** (2001).

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Drug contamination of US paper currency

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Received 3 November 2000; received in revised form 22 December 2000; accepted 8 January 2001

Abstract

It is known that US paper currency in the general circulation is contaminated with cocaine. Several mechanisms have been offered to explain this finding, including contamination due to handling during drug deals and the use of rolled up bills for snorting. Drug is then transferred from one contaminated bill to others during counting in financial institutions. The possibility of contamination of currency with other drugs has not been reported. In this study, the author reports the analysis of 10 randomly collected US$ 1 bills from five cities, for cocaine, heroin, 6 acetylmorphine (6 AM), morphine, codeine, methamphetamine, amphetamine and phencyclidine (PCP). Bills were immersed in acetonitrile for 2 h prior to extraction and GC MS analysis. Results showed that 92% of the bills were positive for cocaine with a mean amount of 28.75 ± 139.07 μg per bill, a median of 1.37 μg per bill, and a range of 0.01 922.72 μg per bill. Heroin was detected in seven bills in amounts ranging from 0.03 to 168.50 μg per bill: 6 AM and morphine were detected in three bills; methamphetamine and amphetamine in three and one bills, respectively, and PCP was detected in two bills in amounts of 0.78 and 1.87 μg per bill. Codeine was not detected in any of the US$ 1 bills analyzed. This study demonstrated that although paper currency was most often contaminated with cocaine, other drugs of abuse may be detected in bills.

Keywords: Contamination; Currency; Cocaine; Heroin; Methamphetamine; Phencyclidine

1. Introduction

In recent years, several studies published in the US have reported the detection of cocaine in the US money supply [1,2]. These studies have demonstrated the presence of cocaine on US$ 1 bills [2] and also US$ 20 bills [3]. Although US paper currency is likely to become contaminated during drug deals, the major source of contamination is considered to be drug users who roll up the currency in order to snort cocaine. As the money is counted in machines in banks, so the machines may become contaminated and transfer small amounts of drug to subsequent bills. Concern has been raised in law enforcement circles as how to differentiate this contaminated money from currency used in drug transactions. Quantities of cocaine detected on randomly collected bills have been low, ranging from 0 to 1327 μg per bill [2]. Studies documented in the literature to date have only tested for the presence of cocaine on currency and have not considered other drugs of abuse such as heroin and phencyclidine. With the reported increase in heroin use (especially by the snorting and smoking routes of administration) [4]; the increase in methamphetamine use [5], and the continued regional use of phencyclidine [6]; a study was conducted to ascertain the contamination of US paper currency with these drugs in addition to cocaine.

2. Experimental

2.1. Chemicals and drug standards

All organic solvents such as methanol, ethyl acetate and acetonitrile, were HPLC grade; all other chemicals were ACS grade. Derivatizing reagents were obtained from Pierce Chemical Company (Rockford, IL). Amphetamine hydrochloride, methamphetamine hydrochloride, and chlorphentermine were purchased from Alltech Applied Science (State College, PA).

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PII: S0379 0738(01)00401 7

2.2. Collection of dollar bills

Paper currency in US$ 1 denominations were collected randomly from four US cities, namely, Baltimore, Chicago, Denver, and Honolulu and also from San Juan, Puerto Rico. The money was in general circulation at the time. Upon collection, the bills were placed in plastic storage bags and stored at room temperature until analysis. Analysis was performed at the Addiction Research Center, Intramural Research Program, National Institute on Drug Abuse, National Institutes of Health, Baltimore, MD, USA.

2.3. Extraction

Each bill (10 from each city) was placed separately in a 15 ml centrifuge tube and 5 ml of acetonitrile was added. Each tube was capped and agitated by vortexing for 4 × 30 s period over 2 h. After 2 h, the bills were removed and aliquots (1 ml for each assay) removed from each tube for analysis. Acetonitrile was used as a drug free control.

2.4. Analysis

Samples were assayed for cocaine, phencyclidine and codeine by modification of a previously published method using solid phase extraction (SPE) followed by gas chro matographic mass spectrometric (GC MS) analysis [8]. An eight point standard curve was assayed in duplicate with each run in a concentration range of 3.1 1000 ng/ml for cocaine, 2.5 500 ng/ml for codeine, and 1.25 250 ng/ml for phencyclidine. Samples were diluted when necessary to ensure the analyte concentration fell within the range of the standard curve. Control samples were assayed with each run at concentrations of 100 and 500 ng/ml cocaine, 25 and 250 ng/ml codeine, and 12.5 and 125 ng/ml for PCP. In addition, a commercially prepared EMIT® II (Syva Co., San Jose, CA) calibrator (300 ng/ml) and an in house 500 ng/ml cocaine hydrolysis control was assayed with each run. The limit of detection was approximately 1.0 ng/ml for each analyte.

Samples were assayed for heroin, 6 acetylmorphine and morphine using a previously published method [7]. A six point standard curve was assayed with each run in a con centration range of 2.5 50 ng/ml. Samples were diluted when necessary to ensure the analyte concentration fell within the range of the standard curve. Control samples were assayed with each run at a concentration of 15 ng/ml. The limit of detection (LOD) and quantitation was approxi mately 1.0 ng/ml for each analyte.

Samples were assayed for methamphetamine and amphetamine by SPE followed by GC MS operated in the SIM mode. Briefly, paper currency acetonitrile extracts, standards and controls were vortexed with 1 ml 0.1N sodium hydroxide and chlorphentermine internal standard solu tion. After mixing for approximately 30 s the samples were applied to SPE columns (Chem Elut™, Varian Corp., 10 ml capacity). The sample tubes were rinsed with 1 ml sodium hydroxide which was applied to the column. The samples were allowed to pass through the columns under gravity. After 10 min the drugs were eluted by adding 2 × 8 ml methylene chloride to each column. After elution, 100 μl 0.1N hydrochloric acid in methanol was added and the methylene chloride evaporated to dryness at 40°C. Extracts were reconstituted with 100 μl chlorobutane and 25 μl chlorodifluoroacetic anhydride, vortexed and heated at 70°C for 10 min. Then 10 μl of 1% hydrochloric acid in acetonitrile was added to each tube, the extracts evapo rated to dryness at 40°C and the residue reconstituted in 500 μl ethyl acetate. A four point standard curve was assayed with each run in a concentration range of 500 5000 ng/ml. A negative control and positive control (2000 ng/ml) were assayed with each run. The limit of detection and quantitation was approximately 100 ng/ml for each analyte.

2.5. Instrumentation

Analyses were performed using a Hewlett Packard 5890A gas chromatograph with an autosampler (HP 7673A) interfaced with a HP 5971A or HP 5970 mass selective detector operated in the SIM mode. A splitless capillary inlet system and a HP 1 fused silica column (12 m × 0.2 mm i.d., 0.33 μm film thickness) was utilized for the amine, cocaine, codeine, phencyclidine analyses. A Restek 5 capillary column (15 m × 0.25 mm i.d., 0.10 μm film thickness) was used for the heroin, 6 acetylmorphine and morphine assay.

3. Results

Drugs were identified by comparison of retention time of the peak of the unknown with the calibrators and the presence of characteristic ions. The cocaine data is presented according to region of bill collection (Table 1). Codeine was not detected in any of the dollar bills analyzed.

3.1. Baltimore

Cocaine was detected in all 10 bills of currency collected in Baltimore. The amount of cocaine detected in each bill was variable, ranging from 0.01 to 13.05 μg per bill. Mor phine, 6 acetylmorphine, PCP, methamphetamine or amphe tamine were not detected in these bills. However, heroin was detected in two bills, in amounts of 76.5 (#3) and 168.5 μg per bill (#9), respectively.

3.2. Chicago

Cocaine was detected in 60% of the bills ($N = 10$) collected in Chicago, in amounts ranging from 0.02 to 1.27 μg per bill. Heroin was detected in three bills (0.03,

Table 1
Cocaine concentrations in the US$ 1 denomination paper currency from five cities

Bill no.	Cocaine amount (μg per bill)[a]				
	Baltimore	Chicago	Denver	Honolulu	San Juan
1	9.87	0.02	1.21	3.25	1.04
2	13.05	1.10	0.52	0.84	0.36
3	2.64	0.10	1.42	0.54	0.21
4	1.43	0.79	3.25	1.44	3.08
5	0.11	1.27	233.55	7.58	26.72
6	0.01	0.13	8.03	1.52	1.67
7	0.37	ND[b]	0.41	1.32	0.06
8	5.44	ND	0.62	20.81	0.20
9	9.48	ND	2.80	922.72	0.82
10	0.59	ND	2.77	24.74	2.42

[a] Reported to two decimal places.
[b] ND: not detected.

0.14, 8.90 μg per bill, C3 C5) and 6 acetylmorphine (9.22 μg per bill) and morphine (5.51 μg per bill) were detected in one bill (#5). Amphetamine was identified in the amount of 0.85 μg (C2) in one bill. No methampheta mine or PCP were detected.

3.3. Denver

Cocaine was detected in all US$ 1 bills collected in the Denver area, in amounts ranging from 0.41 to 233.55 μg per bill. Nine of the ten bills had amounts of cocaine <10 μg per bill. Of these, three contained cocaine at levels <1 μg per bill. Bills identified as D4 and D5, contained 6 acetylmor phine and morphine in nanogram quantities. Bill D9 con tained 0.03 μg of heroin and also PCP (0.78 μg). Bill number D10 also contained PCP in the amount of 1.87 μg per bill. Methamphetamine was detected in two bills (D8 and D10) from the Denver area at a concentration of 0.55 and 0.60 μg per bill.

3.4. Honolulu

Cocaine was detected in all bills collected in Honolulu at amounts ranging from 0.54 to 922.72 μg per bill. Metham phetamine was detected on one bill (H3) at <1 μg per bill. No heroin, 6 acetylmorphine, morphine, PCP or amphetamine were detected.

3.5. San Juan

Cocaine was detected in all bills collected in San Juan ranging from 0.06 to 26.72 μg per bill. Fifty percent of the bills had amounts of cocaine <1 μg per bill. Heroin was detected at a low level (0.09 μg per bill) in one bill (S2). The other drugs measured were not detected in any of the bills from San Juan.

4. Discussion

Randomly collected US$ 1 bills from five cities were assayed for cocaine, heroin, 6 acetylmorphine, morphine, codeine, methamphetamine, amphetamine and phencycli dine. It was found that 92% (46/50) of the bills were positive for cocaine with the largest amount of cocaine per bill (922 μg) measured in Honolulu (H9). Heroin was detected in seven bills; the highest amount found was in bills collected in Baltimore (76.5 and 168.5 μg). 6 Acetylmorphine and morphine were detected in three bills, one obtained in Chicago and two in Denver. These bills were not the same bills in which heroin was measured. Amphetamine was detected in one bill (0.85 μg). Methamphetamine was detected in three bills or 6% of the samples. PCP was detected in two bills or 4% of the samples; both bills were obtained in Denver.

Studies conducted to date have reported low levels of cocaine on US currency. Hearn [9] reported the presence of trace amounts of cocaine in US currency in 1989. He analyzed 135 bills in denominations of US$ 1 100 obtained from banks in 12 cities across the US. He found cocaine in 131 of the bills with an average amount of 7.3 μg cocaine per bill. In another report, Hudson [10] analyzed notes of all denominations obtained from the Bank of Canada in Regina, Saskatchewan, Canada. Notes were tested for cocaine by GC NPD and GC MS following immersion in ethanol and reconstitution of residues with chloroform. Bupivacaine was utilized as internal standard. Quantitation was achieved by GC MS using electron impact ionization operating the instrument in the selected ion monitoring mode and using the 182 ion for cocaine and the 140 ion for the internal standard. Hudson reported cocaine levels of typically <1 ng per banknote, although there were some outliers which the author noted were obtained from notes which were ‘‘worn and dirty’’ [10]. No apparent difference was noted in the amount of cocaine measured between denominations. The author then analyzed five groups of notes seized as the result of drug investigations. The samples were analyzed and quantitated without use of an internal standard. The author reported average levels of cocaine in these notes ranging from 2.7 to 1069 ng per note. The author concluded that the amount of cocaine detected in the seized currency was >50 times the background level and therefore should be regarded as significant. The current study and the work of Hearn disagree with the results of Hudson as *microgram* quantities of cocaine were measured in notes obtained from the general circulation.

Jourdan and Donnelly [11] used ion mobility spectro metry as a screening tool to detect cocaine on currency in the general circulation. Bills were obtained from urban and rural financial institutions. Cocaine was quantitated using elec trospray LC MS or GC MS using a deuterated internal standard. The initial screening involved scanning US cur rency in aliquots of 10 bills, one side only. If the presence of cocaine was indicated by the ion mobility spectrometer, a

second sample was screened. The second sample was the other side of the original 10 bills or a second set of bills obtained from the same recovery. Results presented from 10 areas representing bills from four states (CA, CT, NY and TX) and Washington, DC showed averages of nano gram quantities of cocaine per bill. Cocaine was not detected in bills obtained from several areas. Of the bills which were positive for cocaine no trend was observed with regard to the amount of cocaine per bill and the denomination. The authors concluded from this part of their study that the upper limit of the general background level for cocaine in currency was 13 ng per bill since >95% of the bills in the study had cocaine levels less than this amount. Jourdan and Donnelly then reported data from 40 cases. The data presented demonstrated that >65% of the submissions contained cocaine at a level <30 ng per bill. The authors concluded by stating they considered any bill containing at least 100 ng cocaine is ''statistically different from the background level of the drug on currency in general circulation'' [11]. Obviously the current study disagrees with the results of Jourdan and Donnelly since several hundred micrograms of cocaine were measured in several US$ 1 bills tested. The different sources of the bills between the studies may offer a partial explanation for the different results. In the Jourdan and Donnelly study the bills were obtained from financial in stitutions. No information was provided in the paper as to how or from whom they were obtained. In the current study the bills were obtained as the result of day to day transactions in stores, restaurants and in fees for admit tance to public sites in each of the cities.

Jourdan and Wang [12] noted that when analyzing cocaine from currency obtained in criminal cases, the FBI requests submission of a control sample of bills obtained from a source that can be considered representing currency in the general circulation in the area. These samples are then tested prior to the questioned specimens. Jourdan and Wang also stated that in a 1994 decision by the ninth Circuit Court of Appeals in US v. US Currency (Alexander) 39 F.3d 1039, the court held that a drug dog ''alert'' on a sum of money is not sufficient probable cause for seizure of the currency as proceeds of drug trafficking. Indeed, several studies have been conducted in order to determine canine specificity and sensitivity for the detection of cocaine contaminated cur rency. Poupko et al. [13] reported the results of studies conducted at the Arkansas Police Department in Fayettes ville, AR, using uncirculated currency contaminated with 1 5000 μg cocaine. Negative controls consisted of uncircu lated currency, drug free as determined by GC MS analysis. All three dogs in the study alerted to the negative controls and had varying results with the positive samples from alerting at 1 μg to no alert until the 500 μg bills. When clean bond paper was utilized as the negative control, none of the dogs alerted to the drug free paper. When the same paper was used contaminated with cocaine, two dogs failed to alert to any contaminated paper. The other two dogs in this study gave varying results. This series of studies questions the significance of a dog alert to currency and suggests the possibility that the dogs are responding to a characteristic of the currency itself rather than the drug.

Another issue to consider with regard to drug contamina tion of currency is whether drug may be transferred from the bills to human skin and absorbed by individuals handling such currency. In a study reported by ElSohly [14] two US$ 1 bills were immersed in powdered coca paste, the loose powder shaken off and the bills given to an individual who was instructed to handle them several times throughout the day. The individual was not permitted to wash the hands but otherwise instructed to perform normal functions. Urine samples were collected and tested by immunoassay. The concentration of benzoylecgonine (BE) in the subject's urine was determined semiquantitatively using the assay calibra tors. Urine samples collected up to 8.5 h after initial hand ling of contaminated currency were negative for BE. Samples collected at 12.5, 18 and 21 h were positive for BE at levels of 72, 36 and 24 ng/ml, respectively. Subsequent samples were negative. Utilizing a 300 ng/ml cutoff con centration, the subject was negative for cocaine metabolite. Therefore, it appears unlikely that cocaine or other drugs identified in this study could be transferred to humans by contact with paper currency in sufficient amounts to produce positive test results from urinalysis.

In summary, this study demonstrated the presence of several drugs of abuse in US currency collected randomly from five cities. It appears that microgram amounts of drug may be present on bills in the general circulation. To the author's knowledge, this is the first report of drug contam ination of US currency with heroin, PCP or methampheta mine. Drug contamination of currency other than US and Canadian dollars has not been reported. It is possible that examination of paper currency from countries with a dif ferent drug abuse problem will demonstrate a varying dis tribution of contamination.

Acknowledgements

The author wishes to thank Mr. Abraham Tsadik of the Drug Chemistry and Metabolism Section, Intramural Research Program, NIDA, NIH, Baltimore, MD for help with the drug analysis.

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Attachment C6

Zuo, Y., Zhang, K., Wu, J., Rego, C., and Fitz, J., An Accurate and Nondestructive GC method for determination of Cocaine on US Paper Currency, *J. Separation Sci.*, **31** (2008).

J. Sep. Sci. 2008, *31*, 2444 2450

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Original Paper

An accurate and nondestructive GC method for determination of cocaine on US paper currency

The presence of cocaine on US paper currency has been known for a long time. Banknotes become contaminated during the exchange, storage, and abuse of cocaine. The analysis of cocaine on various denominations of US banknotes in the general circulation can provide law enforcement circles and forensic epidemiologists objective and timely information on epidemiology of illicit drug use and on how to differentiate money contaminated in the general circulation from banknotes used in drug transaction. A simple, nondestructive, and accurate capillary gas chromatographic method has been developed for the determination of cocaine on various denominations of US banknotes in this study. The method comprises a fast ultrasonic extraction using water as a solvent followed by a SPE cleanup process with a C_{18} cartridge and capillary GC separation, identification, and quantification. This nondestructive analytical method has been successfully applied to determine the cocaine contamination in US paper currency of all denominations. Standard calibration curve was linear over the concentration range from the LOQ (2.00 ng/mL) to 100 μg/mL and the RSD less than 2.0%. Cocaine was detected in 67% of the circulated banknotes collected in Southeastern Massachusetts in amounts ranging from ~2 ng to 49.4 μg *per* note. On average, \$5, 10, 20, and 50 denominations contain higher amounts of cocaine than \$1 and 100 denominations of US banknotes.

Keywords: Cocaine / Gas chromatography – flame ionization detection – mass spectrometry / Paper currency / Solid phase extraction / Ultrasonic extraction

Received: March 2, 2008; revised: April 1, 2008; accepted: April 2, 2008

DOI 10.1002/jssc.200800117

1 Introduction

Cocaine, 3-benzoyloxy-8-methyl-8-azabicyclo[3.2.1]octane-2-carboxylic acid methyl ester (Fig. 1), is one of the most commonly abused illicit drugs in the world. In the US alone, 6 million people report using cocaine annually on a regular basis, consuming between 259 and 447 metric tons of cocaine at a cost of US\$ 35 70 billion [1, 2]. Cocaine abuse transcends all social, racial, and economic boundaries. Many cocaine users use a wrapped banknote to sniff this drug. It has been known since the mid 1980s that paper currencies in North American and European countries are contaminated with cocaine residue during the drug deals and consumption [3]. The presence of trace levels of illicit drugs on banknotes is frequently used as a part of the forensic evidence to establish a link between a suspect to these drugs [4]. Forensic scientists are now also measuring cocaine on paper currencies as a part of an effort to study the epidemiology of illegal drug abuse. For the past few decades, epidemiologists have struggled to obtain a quantitative view of illicit drug use. However, the traditional data such as tons of drugs seized, the number of people seeking treatment for addiction, drug-related mortality, and responses to drug-abuse questionnaires are biased and inaccurate, which makes scientists turn to the environment and believe that the measurement of drugs on the money and in sewage wastewater would provide objective and timely epidemiological information on illicit drug use [5].

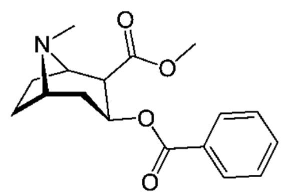

Figure 1. Chemical structure of cocaine.

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Abbreviations: FID, flame ionization detection; **HP,** Hewlett – Packard; **IS,** internal standard; **NPD,** nitrogen – phosphorus detection

Several techniques such as GC coupled with nitrogen phosphorus detection (NPD), MS, positive-ion chemical-ionization MS, atmospheric pressure chemical-ionization MS or MS-MS, Raman microspectroscopy, and CE, for the analysis of cocaine on paper currencies have been reported in the literature [4 14]. Among these techniques, GC-MS has been the most widely employed method. In previous studies, various organic solvents such as chloroform and ACN were used to extract cocaine from banknotes prior to GC-MS analysis which cause damage of the security band and holographic marks [4 9]. Even use of methanol, which has been considered an environmentally friendly nondestructive organic solvent, loosens the metallic foil used to check against counterfeit money [5, 9]. In this study, we have aimed to develop a simple, accurate, and nondestructive procedure for the determination of cocaine on US banknotes using ultrasound-enhanced aqueous extraction and GC-flame ionization detection (FID) and GC-MS detection. A SPE with Supelco Discovery C_{18} cartridges was used to isolate the analyte in aqueous extracts.

2 Materials and methods

2.1 Drug standards, chemicals, and materials

Cocaine, 1.00 mg/mL in ACN drug standard, was purchased from Sigma (St. Louis, Missouri, USA). All organic solvents such as methanol, ethyl acetate, hexane, and chloroform were of HPLC grade from Pharmco Products (Brookfield, NJ, USA). Anthracene was supplied by Eastman Organic Chemicals (Rochester, NY, USA). The water used for the sample extraction and solution preparations was doubly distilled and then de-ionized. All the other chemicals were of analytical reagent grade and were used without further purification. Supelco Discovery SPE C_{18} cartridges coupled with a vacuum system (Bellefonte, PA, USA) were used to isolate aqueous cocaine extract. Prior to extraction, the cartridges were sequentially conditioned with 5.00 mL of hexane, 5.00 mL of ethyl acetate, 5.00 mL of methanol, and 5.00 mL of doubly distilled and de-ionized water.

2.2 Collection of US banknotes

Paper currency in US$ 1, 5, 10, 20, 50, and 100 denominations were collected randomly from cities in Southeastern Massachusetts, USA (New Bedford, Fall River, and Dartmouth). The banknotes were in general circulation at the time. Noncirculated banknotes were obtained directly from an American bank. Upon collection, the notes were placed in plastic storage bags and stored at room temperature until analysis.

2.3 Sample extraction and preparation

Each banknote was placed separately in a 20 mL glass vial and 15 mL of doubly distilled and de-ionized water was added to the vials to completely submerge the note in the water. All vials were capped and sonicated at room temperature for 5 min in an ultrasonic bath (VWR Signature Ultrasonic Cleaner Model 75D, 90 W) with Digital Timer, Heat, and Power (VWR, S. Plainfield, NJ, USA). Aqueous extractant (10 mL) was loaded on a preconditioned C_{18} cartridge. The cartridge was washed with 2.00 mL of distilled water and 2.00 mL of methanol. The analyte was eluted using 5.00 mL of a mixture of methanol, ethyl acetate, and hexane (1:3:1 by volume) into a clean vial and evaporated to dryness at ambient temperature under nitrogen and reconstituted with 475 μL of methanol and 25 μL of internal standard (IS) (0.700 mg/mL anthrancene in methanol) to make a final volume of 500 μL. A second extraction was made on the same banknotes to check the extraction efficiency of the above described procedure by following the same procedure but using methanol instead of water to soak the banknotes.

2.4 Cocaine analysis

GC analysis was carried out on a Shimadzu GC-17A gas chromatograph equipped with a FID, a Shimadzu AOC-20i GC auto-injector, and a Gateway E-4200 computer that utilizes CLASS-VP Chromatography Data System Version 4.2 (Shimadzu Scientific Instruments, Columbia, MD, USA). Samples were separated on a 30 m × 0.32 mm id, 1.00 μm film EC™-5 capillary column (Alltech, Deerfield, IL, USA). The stationary phase was composed of 5% phenyl- and 95% dimethyl-polysiloxane mixture. Helium was employed as a carrier gas with a linear velocity of 27 cm/s. Nitrogen make up gas, hydrogen and compressed air were used for the FID. A split/splitless injector was used in a splitless mode. The injector volume was 2.0 μL. The column temperature was initially held at 80°C for 2 min, then programmed to 200°C at a rate of 40°C/min, then ramped up to 280°C at a rate of 20°C/min, with a final hold time of 3 min. The injector and detector temperature were maintained at 290°C and 310°C, respectively.

The peak identification and purity verification was performed by employing a Hewlett Packard (HP) model GC 5890 Series II gas chromatograph coupled with an HP 5971 series mass selective detector and an HP 7673 GC autosampler [15, 16]. Samples were separated on a DB-5 fused-silica capillary column (30 m × 0.32 mm id, 0.25 μm film, J & W Scientific, Folsom, CA, USA). The column temperature was initially held at 80°C for 3 min, then the temperature was raised to 260°C at a rate of 20°C *per* min. Ultrahigh purity helium with an inline All-

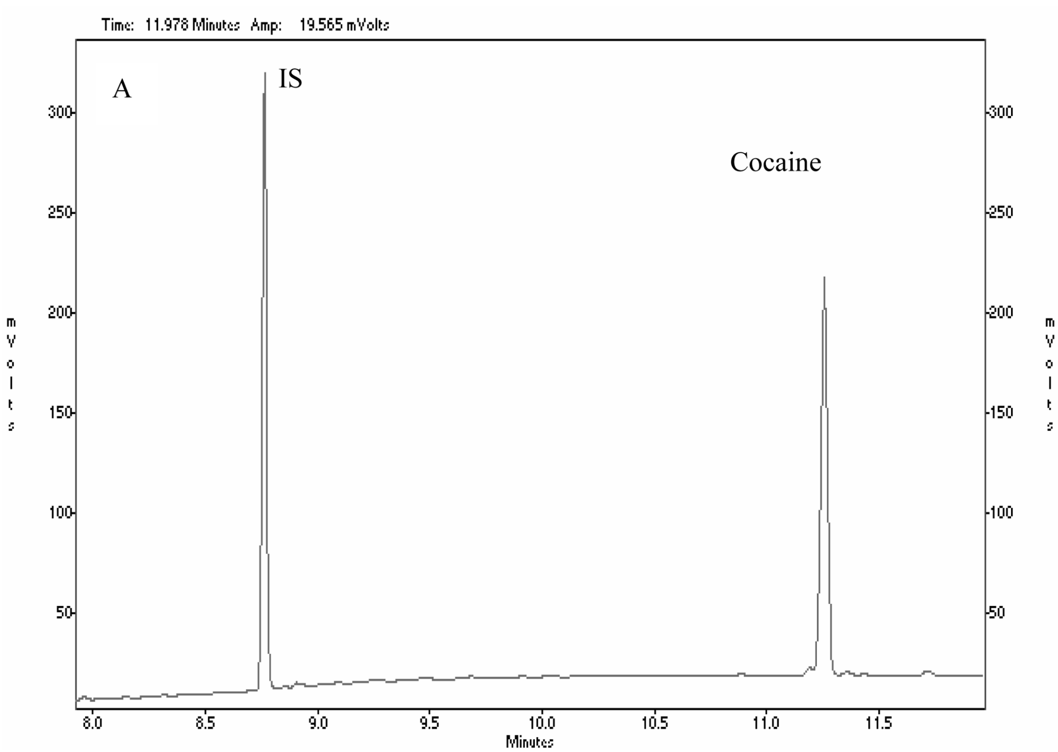
tech oxygen trap was used as a carrier gas with a column head pressure at 3 psi. The injector temperature was maintained at 280°C and the injection volume was 1.0 μL in splitless mode. The interface temperature was held at 305°C. Mass spectra were scanned from m/z 50 to 650 at a rate of 1.5 scans/sec. Identification of cocaine was performed by comparing the retention time of the suspect peak with that of an authentic cocaine standard and its mass spectra. The quantification of cocaine was based on the ratio of the peak area of cocaine over the peak area of the IS.

3 Results and discussion

3.1 Extraction of cocaine from banknotes

Prior to using GC coupled with an FID or MS detector for the determination of cocaine extracted from banknotes, the efficacy of the separation and detection of cocaine was tested on a standard mixture of cocaine and the IS. The instrument parameters such as the temperature program and carrier gas flow rate, were optimized to obtain a good resolution between cocaine, IS, and possible components in the extract matrix. Figure 2A illustrates a clean separation of cocaine and the IS with a retention time of 8.77 ± 0.1 min for the IS and 11.3 ± 0.1 min for cocaine using the method described.

The separation and quantification of cocaine in circulated paper currency is more difficult due to the chemical complexity of banknote contaminants. In previous studies, several organic solvents including chloroform, ACN, and methanol have been used to extract cocaine from contaminated banknotes successfully because of the high solubility of cocaine in the organic solvents [4 9]. However, the use of these organic solvents causes a damage to the security band and/or holographic marks of banknotes [5, 9]. Furthermore, in some of the previous studies without a cleanup process for the organic solvent extracts, the contaminants such as ink, grease, oil, cosmetics, *etc*. on the paper currency resulted in a large amounts of peaks in the chromatogram, overlapping the cocaine peak. Cocaine is an alkaloid base with a pK_a of 8.6 and has a solubility of 0.17 g/100 mL in water at room temperature; its salt, typically cocaine hydrochloride, the most popular powder form of street market cocaine, has a solubility of 250 g/100 mL in water at 20°C. It is therefore possible to avoid the destruction of paper currency in the analytical processes by using water instead of an organic liquid as a solvent to extract cocaine. Water as an extraction solvent preferably extracts hydrophilic components such as cocaine salt but not hydrophobic compounds, which interfere the determination of cocaine as encountered in the previous studies using organic extraction solvents. Recent studies have shown that the application of ultrasound wave can tremen-



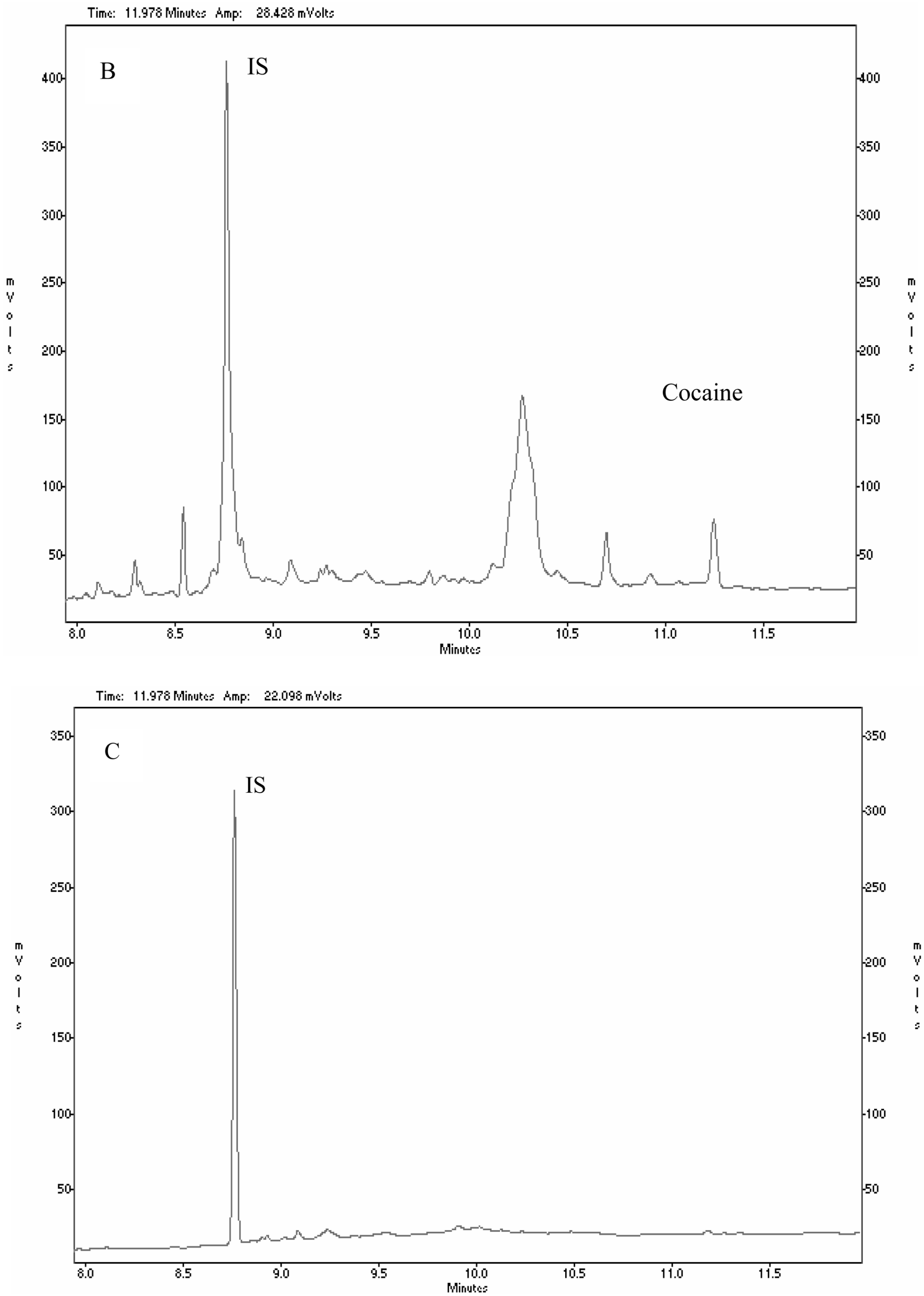


Figure 2. GC chromatogram. (A) Chromatogram of a mixture solution of cocaine standard and IS; (B) Chromatogram of water extract of a $20 banknote (Table 1, banknote no. 21); (C) Chromatogram of the second extract of the same banknote with methanol after the first aqueous extraction.

dously speed up liquid liquid extraction [17 20] and thus can also be used to enhance the aqueous extraction of cocaine from the banknotes. A SPE with Supelco Discovery C_{18} cartridges was employed to isolate the analyte in aqueous extracts to ensure reliable identification and quantification in this study.

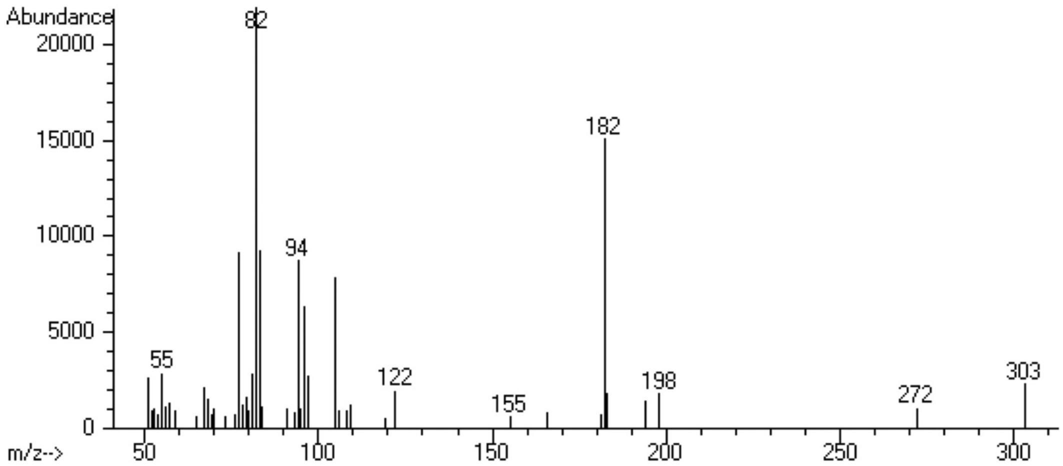


Figure 3. Mass spectrum of cocaine.

In order to evaluate the efficiency of the extraction procedure, a series of banknotes were first extracted as described with water as a solvent. A second extraction was then made on the same banknotes by following the same procedure but using methanol instead of water to submerge the notes. Typical chromatograms from the first and second extracts of a circulated banknote are presented in Fig. 2, panels B and C. Figure 3 shows a typical mass spectrum of cocaine. The characteristic ions of cocaine at *m/z* 303 (molecular ion, $[M]^+$), 272 (ion attributed to α-cleavage product, $[M \quad OCH_3]^+$), 182 (ion corresponding to $[M \quad C_6H_5COO]^+$), and 82 (ion attributed to α-cleavage product, $[C_4H_5NCH_3]^+$) provide unequivocal evidence of the identity of cocaine on the banknotes examined. No detectable cocaine was observed in the second extracts, indicating a single extraction with water is sufficient to remove all cocaine from the notes.

The recovery experiments were performed by adding 100 μL of 0.100 mg/mL of cocaine standard solution to noncirculated banknotes. The cocaine-spiked banknotes were extracted with water or methanol, as a comparison to previous studies, and subjected to the entire analytical procedure with the samples in triplicate. The results are given in Fig. 4. A good percentage recovery of 95 ± 2% was obtained for a single extraction with either water or methanol as a solvent. Water was chosen as an extraction solvent because it does not cause any damage to the banknotes.

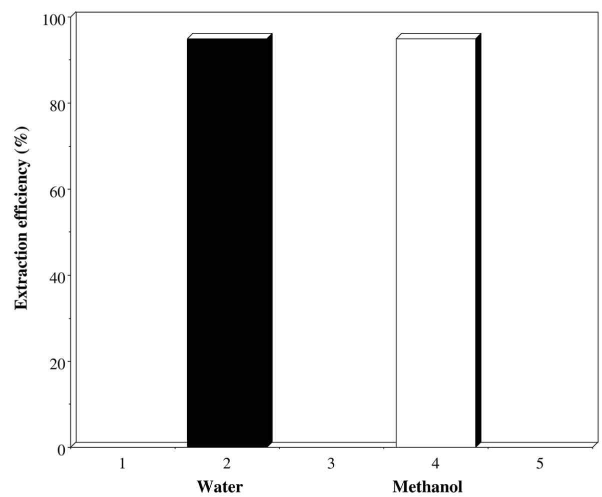


Figure 4. Extraction efficiency of cocaine in paper currency with water and methanol (relative error: ±2%).

3.2 Method validation

A calibration curve was obtained for cocaine using a series of standard solutions over the concentration range from 0.00 to 100 μg/mL. Three replicate injections of each standard solution were performed. The standard curve was linear over the concentration range tested and had the square of the correlation coefficient, slope, and intercept of 0.994, $1.33 \times 10^{\ 2}$, and $2.85 \times 10^{\ 3}$, respectively. The LOQ was 4 ng of cocaine *per* banknote, which was established as the concentration of cocaine that gives rise to peak height with a S/N of 10.

The reproducibility of the retention time for the IS and cocaine was determined from 25 consecutive injections during an analysis of a series of cocaine samples. The RSD%) was found to be less than 0.02%. The precision in the peak area ratio of cocaine over the IS was better than 1.0% for ten consecutive injections of the same cocaine sample. Repeatability of the method was performed by six analysts (five determinations by each analyst) using the proposed method and the same instrumentation. The results showed no significant differences: RSD% less than 2.0.

Table 1. Amounts of cocaine in various denominations of US paper currency collected in Southeastern Massachusetts

Denomination	Banknote no.	Amount of cocaine (μg/note)[a)]
1$	1 5	ND[a9]
5$	6	49.4
	7	16.5
	8	12.8
	9	12.4
	10	4.65
10$	11	46.2
	12	6.74
	13	8.57
	14	4.05
	15	6.57
	16	Trace[b)]
	17	ND
20$	18	7.20
	19	9.21
	20	3.66
	21	5.14
	22	Trace
	23	ND
50$	24	19.6
	25	15.9
	26	14.1
	27	3.82
100$	28	ND
	29	8.87
	30	ND
	31	ND

a) Not detected.
b) Below LOQ.

3.3 Analysis of cocaine in paper currency

The described method has been applied to extract and determine cocaine in various denominations of the United States banknotes collected in City New Bedford, Fall River, and Dartmouth all in Southeastern Massachusetts. The analytical results are listed in Table 1. Cocaine was detected in 67% of the circulated banknotes (N = 31), in amounts ranging from ~2 ng to 49.4 μg *per* note. All extracts from $5 and $50 banknotes were positive for cocaine; the amount of the drug was between 4.65 and 49.4 μg *per* note with an average of 19.2 μg *per* note in $5 notes, and between 3.82 and 19.6 μg *per* note with an average of 13.4 μg *per* note in $50 notes. Seven $10 notes were analyzed; one note was negative and another contained traces of cocaine (below quantification limit); the average level of cocaine in $10 notes was 10.3 μg *per* note. Six $20 notes were detected; one was negative, four positive, and one had trace level of cocaine with an average of 4.20 μg *per* note in $20 denomination. Cocaine was found in only one of the four $100 bills with an average level of 2.22 μg *per* note and in none of the five $1 notes. All unused banknotes (N = 10) of various denominations were negative for cocaine. To the best of our knowledge, this is the first study that analyzed cocaine in US banknotes of all denominations.

Several previous studies have reported cocaine contamination on US currency. Oyler *et al*. [6] have analyzed $1 notes collected from several US cities and found that cocaine was present in 79% of the currency samples analyzed in amounts above 0.1 μg. Jenkins [7] reported the presence of cocaine in 92% of US$1 bills randomly collected from five US cities in a range of 0.01 922.72 μg *per* bill with a mean amount of 28.75 ± 139.07 μg *per* bill. Negrusz *et al*. [8] examined ten $20 banknotes from Rockford (IL, USA) and four $1 notes from Chicago. They observed that cocaine was present on 92.8% of all notes; all $20 notes were contaminated with cocaine and the amount of drug varied from 0.14 to 10.02 μg of cocaine *per* bill; only one $1 note was cocaine free; one contained only traces of cocaine (below quantitation limit). Most of the previous studies of cocaine contamination on US currency have focused on $1 denomination because it was believed that no apparent difference in the amount of cocaine contaminant between denominations. In this study, however, cocaine was not detected in any of the five $1 bills but in all other denominations of the US banknotes. It is also interesting to note from the current study that the average amount of cocaine in the $1 and $100 denominations were significantly lower than in other denominations of the US paper currency collected in the Southeastern Massachusetts. When analyzing cocaine from currency obtained in criminal cases, the Federal Bureau of Investigation (FBI) requests submission of a control sample of banknotes obtained from a source that can be considered representing currency in the general circulation in the area. In the light of this study, the denominations should be considered when colleting a control sample of banknotes in criminal investigation of cocaine related money.

4 Concluding remarks

A simple, nondestructive, and accurate ultrasound-enhanced aqueous extraction and capillary GC-FID/MS method has been developed and validated for the determination of cocaine in US paper currency. The results obtained in this study indicate that ultrasound-enhanced extraction with water as a solvent was at least as efficient as with methanol and water did not cause any damage to the banknotes. This study has also demonstrated the presence of cocaine in various denominations of US paper currency collected randomly in Southeastern Massachusetts and the average levels of cocaine on $1 and $100 denominations were significantly lower than on other denominations of banknotes. To the authors' knowledge, this is the first report of cocaine contamination on the US paper currency of all denominations.

The authors thank Dr. W. Dills, C. Wang, G. Desmond, X. Feng, Y. Jiao, C. Moon, O. Onayemi, and T. Van for their contribution and assistance to this work. This research was partly supported by the Department of Chemistry and Biochemistry, University of Massachusetts Dartmouth.

The authors declared no conflict of interest.

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Attachment C7

Zuo, Y., et.al., Unpublished presentation to the American Chemical Society.
ACS Press Release and Scientific American Article attached

ACS
Chemistry for Life

EMBARGOED FOR RELEASE| **August 16, 2009**

New study: Up to 90 percent of U.S. paper money contains traces of cocaine

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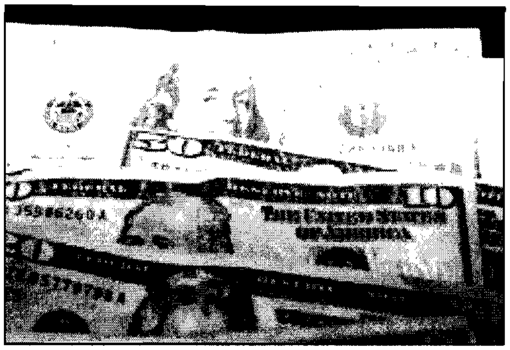
WASHINGTON, Aug. 16, 2009 — You probably have cocaine in your wallet, purse, or pocket. Sound unlikely or outrageous? Think again! In what researchers describe as the largest, most comprehensive analysis to date of cocaine contamination in banknotes, scientists are reporting that cocaine is present in up to 90 percent of paper money in the United States, particularly in large cities such as Baltimore, Boston, and Detroit. The scientists found traces of cocaine in 95 percent of the banknotes analyzed from Washington, D.C., alone.

Presented here today at the 238th National Meeting of the American Chemical Society, the new study suggests that cocaine abuse is still widespread and may be on the rise in some areas. It could help raise public awareness about cocaine use and lead to greater emphasis on curbing its abuse, the researchers say.

The scientists tested banknotes from more than 30 cities in five countries, including the U.S., Canada, Brazil, China, and Japan, and found "alarming" evidence of cocaine use in many areas. The U.S. and Canada had the highest levels, with an average contamination rate of

between 85 and 90 percent, while China and Japan had the lowest, between 12 and 20 percent contamination. The study is the first report about cocaine contamination in Chinese and Japanese currencies, they say.



Traces of cocaine exist in up to 90 percent of banknotes in many large U.S. cities, a new study reports.
Credit: The American Chemical Society
High-resolution version

"To my surprise, we're finding more and more cocaine in banknotes," said study leader Yuegang Zuo, Ph.D., of the University of Massachusetts in Dartmouth.

Zuo says that the high percentage of contaminated U.S. currency observed in the current study represents nearly a 20 percent jump in comparison to a similar study he conducted two years ago. That earlier study indicated that 67 percent of bills in the U.S. contained traces of cocaine.

"I'm not sure why we've seen this apparent increase, but it could be related to the economic downturn, with stressed people turning to cocaine," Zuo says. Such studies are useful, he noted, because the data can help law enforcement agencies and forensic specialists identify patterns of drug use in a community.

Scientists have known for years that paper money can become contaminated with cocaine during drug deals and directly through drug use such as snorting cocaine through rolled bills. Contamination can spread to banknotes not involved in the illicit drug culture because bills are processed in banks' currency-counting machines.

Previous studies on cocaine in banknotes, however, had several drawbacks. They often were based on sampling only a small number of banknotes, for instance. Some tests destroyed the currency.

In the new study, Zuo and colleagues describe use of a modified form of a standard laboratory instrument termed a gas chromatograph-mass spectrometer. It allows a faster, simpler and more accurate measurement of cocaine contamination than other methods, without destroying the currency. The researchers used the method to analyze banknotes of several different denominations from the five countries surveyed.

The U.S. had the highest levels. The scientists analyzed a total of 234 banknotes from the U.S. and found that up to 90 percent of the banknotes contain traces of cocaine. Amounts ranged from .006 micrograms (several thousands of times smaller than a single grain of sand)

to over 1,240 micrograms of cocaine per banknote (about 50 grains of sand). For comparison: A grain of sand weighs approximately 23 micrograms; there are one million micrograms in a gram and 28 grams in an ounce.

The scientists collected U.S. banknotes from 17 U.S. cities and found that larger cities like Baltimore, Boston, and Detroit had among the highest average cocaine levels. Washington, D.C., ranked above the average, with 95 percent of the banknotes sampled contaminated with the drug. The lowest average cocaine levels in U.S. currency appeared in bills collected from Salt Lake City.

The researchers studied 27 banknotes from Canada and found that 85 percent were contaminated with cocaine, with amounts ranging from 2.4 micrograms to over 2,530 micrograms of coke per banknote. The researchers analyzed 10 banknotes from Brazil and found that 80 percent were contaminated with cocaine, still high but lower than the U.S. and Canada.

China and Japan had the lowest levels. The researchers analyzed 112 banknotes from China and found that about 20 percent were contaminated with cocaine. Of the 16 banknotes analyzed from Japan, only about 12 percent were contaminated with cocaine, the researchers say.

Despite the high percentage of cocaine-contaminated banknotes, Zuo points out that the amount of cocaine found on most notes was so small that consumers should not have any health or legal concerns about handling paper money.

"For the most part, you can't get high by sniffing a regular banknote, unless it was used directly in drug uptake or during a drug exchange," Zuo said. "It also won't affect your health and is unlikely interfere with blood and urine tests used for drug detection." This study was partly funded by the University of Massachusetts-Dartmouth.

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— Mark T. Sampson

SCIENTIFIC AMERICAN

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News | Health

Cocaine Contaminates Majority of U.S. Currency

And it's not just the U.S.: Canada and Brazil have a preponderance of the drug powder on their bills, too

By David Biello |August 16, 2009 | 30

For cocaine users, a rolled up $20 bill may be the most convenient tool for snorting the powder form of the drug. Or so it would seem from a new analysis of 234 banknotes from 18 U.S. cities that found cocaine on 90 percent of the bills tested.

Perhaps that's not surprising given that the U.S. Office of National Drug Control Policy reports that more than 2 million Americans used cocaine in 2007, which has been linked to ill effects ranging from debilitating addiction to heart attacks. The United Nations Office on Drugs and Crime, for its part, reported in the same year that 6 million Americans admit using cocaine annually, consuming a total of as much as 457 metric tons in a year.

"Cocaine is a powerfully addictive stimulant and one of the most commonly abused illicit drugs in the world," says chemist Yuegang Zuo of the University of Massachusetts Dartmouth, who conducted the tests and presented the findings today at the biannual meeting of the American Chemical Society, which is taking place in Washington, D.C. That city ranked highest in the survey—95 percent of the sampled bills there bore cocaine contamination—along with Baltimore, Boston and Detroit. Salt Lake City had the lowest average levels of contamination. "The examination of cocaine contamination on paper money can provide objective and timely epidemiological information about cocaine abuse in individual communities," Zuo argues.

What might be more surprising is the fact that the percentage of contaminated bills seems to be rising; just two years ago, Zuo did a similar study that found cocaine on only 67 percent of banknotes in Massachusetts. "It is too early to draw a conclusion about why," Zuo says. "The economic downturn may partly contribute to the jump."

But the U.S. Drug Enforcement Administration (DEA) notes that other measures, such as pretrial urine samples from defendants accused of crimes, show that drug use, at least in the D.C. area, has gone down slightly—only 29 percent of adult arrestees had traces of cocaine in their urine in the first six months of 2009, the lowest level since 1985. "We know that cocaine prices have gone up significantly in the last two years, which usually deters use of that drug," says special agent Melissa Bell of the Washington, D.C., division office of the DEA. "Junkies go on to use something cheaper."

Levels of cocaine ranged from .006 micrograms to more than 1,240 micrograms—the equivalent of 50 grains of sand—on U.S. bills, and $5, $10 and $20 bills on average carried more contamination than $1 or $100 bills.

Zuo and his colleagues also tested banknotes from Brazil, Canada, China and Japan, and found that Asians appear to use the drug less—only 20 percent of the 112 Chinese renminbi notes tested had traces, and only 12 percent of 16 Japanese yen notes tested bore the drug.

But Canadians seem to be just as fond and, perhaps, a bit sloppier in their consumption or dealing. More than 2,350 micrograms of cocaine were found on some of the Canadian bills, 85 percent of which had some level of contamination, while 80 percent of Brazilian reals also bore traces of the drug.

Whether this means drug use is on the rise or that ATMs and other bulk cash-handling machines—where one contaminated bill can spread powder to many others—are ever more ubiquitous cannot be discerned. "It is still difficult to tell quantitatively how much is due to primary contamination, such as during a drug deal or [use], and how much is due to secondary contamination, such as interaction between contaminated and uncontaminated bills," Zuo says. "Both may contribute ... [but] it seems clear that the banknotes containing 1,240 micrograms of cocaine were used directly during a drug deal or uptake [drug use]."

Previous studies, stretching as far back as 1987, have found varying levels of cocaine contamination, some even higher than the new finding. But Zuo is the first to analyze foreign banknotes for contamination and the first to employ a new method of gas chromatography, which detects the chemical signature of the drug without damaging the actual money, to do the analysis.

The finding might complicate an anti-drug dealing tactic used by the Federal Bureau of Investigation (FBI) and other enforcement agencies, Zuo says. In some cases, the FBI compares the levels of cocaine contamination on seized bills to levels found on bills in general circulation, treating this as evidence. "Sometimes [drug dealers] use these studies to try to get their money back when we seize it," Bell notes. But the DEA's drug-sniffing dogs are not actually detecting cocaine; they are sensing a chemical used in its manufacture that dissipates more quickly. "So they don't get their money back," Bell says.

Regardless, it would seem, according to this research, that C-notes are not as popular with drug dealers (or users) as perhaps popularly depicted. "You rarely see them breaking out the hundreds unless they're buying kilos," Bell adds. "The user on the street is going to be breaking out the five, ten or twenty."

Attachment C8

Dejarme, L.E., Gooding, R.E., Lawhon, S.J., Ray, P., and Kuhlman, M.R., Formation of Methyl Benzoate from Cocaine hydrochloride under Different Temperatures and Humidies, *Proceedings. SPIE*, **2937:**19 (1996).

The formation of methyl benzoate from cocaine hydrochloride under different temperatures and humidities

Lindy E. Dejarme, Rachel E. Gooding, Sara J. Lawhon, Prasenjit Ray, Michael R. Kuhlman

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ABSTRACT

It is of interest for drug enforcement agencies to know the fate of cocaine hydrochloride when in storage. Reported here are results obtained on vapor samples collected from cocaine hydrochloride stored under several combinations of temperature and humidity. The storage conditions were varied from ambient temperature to 40°C and from zero humidification to 80% relative humidity. Cocaine hydrochloride samples (approximately 300 mg each) were coated onto glass beads and loaded into a glass reactor (fitted with a glass frit) which was in turn placed inside a heated metal chamber. Ultra-zero air, conditioned to the desired humidification, was purged into the glass container, through the glass frit, over the coated beads, and the exit gas was collected onto a sorbent tube packed with Tenax TA. Any chemical product arising from the interaction between cocaine hydrochloride and the flowing air was effectively collected onto the sorbent tube, which was analyzed using a split column GC/MS technique. The results of these storage experiments showed that methyl benzoate is a predominant volatile product, even at zero percent humidification. The average formation of methyl benzoate was found to range from 1.89 ng/min with ambient/dry conditions after one hour to 62 ng/min at 40°C/80% RH upon introduction of flowing air. These results indicate that cocaine hydrochloride exposed to any realistic humidity level in the environment will produce methyl benzoate, a volatile organic material which can be much more readily detected than cocaine hydrochloride itself.

Keywords: plug flow reactor, cocaine hydrochloride, split column, GC/MS analysis, methyl benzoate, sorbent tube

1. INTRODUCTION

Cocaine hydrochloride is among one of the many substances of abuse used by people regardless of their economic status. Also associated with the illicit use of cocaine hydrochloride is crime. The rampant use and seemingly continuous supply of cocaine hydrochloride is due, in part, to improvements made by smugglers in their techniques of hiding and transporting cocaine hydrochloride from one place to another. To reduce drug trafficking of cocaine hydrochloride, efforts are being made to understand volatile components that are traceable to cocaine hydrochloride. It is in this context that this study is being conducted.

Despite the large body of literature available on cocaine hydrochloride, which includes description of its physical properties,[1] impurities,[2] stability of the substance in aqueous media[3], and stability at different pH conditions,[4] no research has determined the fate of cocaine hydrochloride during storage. Hence, the objective of this study is to investigate the chemical reactivity of cocaine hydrochloride under different storage conditions, that is, different humidity and temperature conditions. This study is focused on the volatile components that are released from cocaine hydrochloride under selected environmental conditions. Although this work has not yet been completed, the experimental design and preliminary results are reported.

2. TECHNICAL APPROACH

Four main areas were considered when designing the experimental apparatus; the design of the reaction vessel, the conditioning unit, sampling of volatile materials, and the analytical method used to analyze the volatile components. Two experimental apparatuses were tested for conducting the cocaine hydrochloride storage experiments. The configuration and operation of each experimental apparatus, sampling and analytical methods are discussed below. The advantage of one experimental setup over another is discussed in the Results section of this manuscript.

2.1. Experimental apparatus for the zero flow reactor (ZFR)

Fig. 1 displays the schematic diagram for the experimental apparatus using a zero flow reactor. The volatile products from this reactor were collected and analyzed using the equipment in Fig. 2.

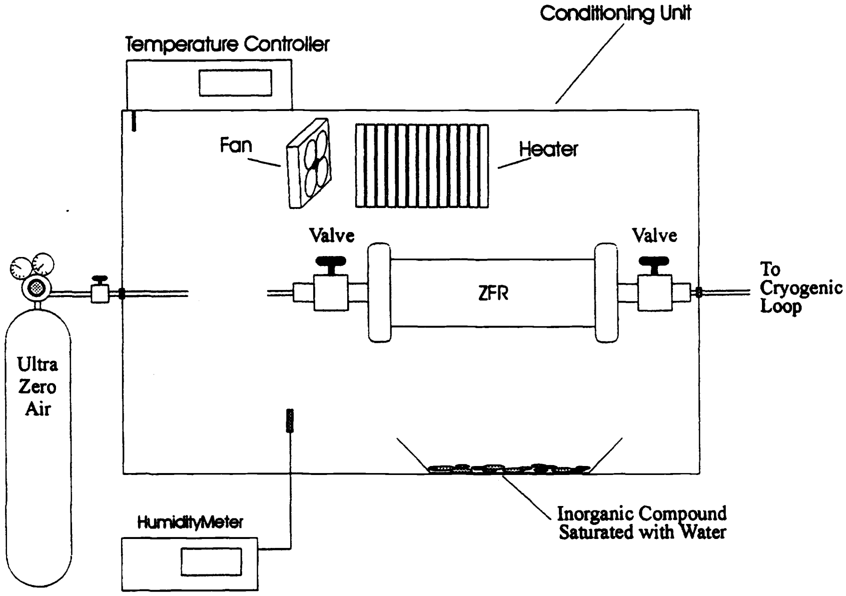

Fig. 1. Schematic diagram for the experimental setup to conduct the cocaine hydrochloride storage experiment using a zero flow reactor (ZFR)

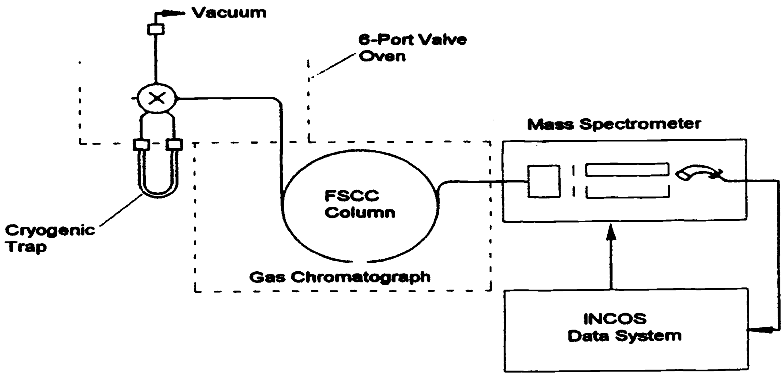

Fig. 2. Configuration of the sampling device and the GC/MS instrument

A glass boat (not shown in the diagram), shaped like a bottle with both ends tapered and open, was encased in a metal cylinder equipped with open/close valves at each end (labeled ZFR, Fig. 1). A measured amount of pharmaceutical grade cocaine hydrochloride was placed inside the glass boat which was then placed on its side in the metal cylinder. The metal cylinder was evacuated with a mechanical pump to remove any volatile components that were inadvertently admitted into the reactor when the cocaine hydrochloride was loaded. The temperature in the conditioning unit, constructed from plexiglas, was equilibrated to the designated experimental temperature. If humidification was required, an inorganic compound saturated with water, which maintained a specific chamber humidity, was placed inside the conditioning unit. Once thermal equilibration was achieved, the reactor was opened to the conditioned environment thus admitting the environmentally conditioned ultra zero air inside the reactor. The valve was closed and the contents of the reactor were incubated.

The volatile components released in the reactor were purged into a cryogenic loop maintained at liquid nitrogen temperature (see Fig. 2) with Ultra High Purity helium. The contents of the cryogenic loop were then thermally desorbed into the GC capillary column maintained at subambient temperature to effect cryofocusing of the volatile components. GC/MS analysis (using a Finnigan 4500 GC/MS instrument equipped with a 60 meter DB-5 column) was started once the desorption process was complete.

2.2. Experimental apparatus for the plug flow reactor (PFR)

Fig. 3 shows the schematic diagram of the experimental apparatus using a plug flow reactor (PFR). The plug flow reactor consisted of an upright glass vessel fitted with a glass frit at the bottom. Cocaine hydrochloride coated glass beads were loaded into the PFR which was then inserted into the stainless steel heater. The purge gas for these experiments, ultra zero air, was either dried with calcium carbonate or humidified before it was admitted into the PFR. Humidification for this setup was achieved by flowing water through a Nafion tubing while the exterior of the tubing was swept continuously with ultra zero air. The humidity of the ultra zero air was controlled by varying the amount of unhumidified ultra zero air mixed with the humidified portion. Volatile materials that were produced in the PFR were collected using sorbent tubes packed with Tenax TA. The Tenax TA sorbent was selected as the sorbent bed because of its high affinity for organics and absence of affinity for water.

The sorbent tubes were analyzed off-line using a Finnigan 4500 GC/MS instrument equipped with 30 meter DB-5 column. The GC capillary column was set up as a split column configuration[5] as shown in Fig. 4.

3. RESULTS

Fig. 5 is a GC/MS chromatogram displaying the results from the cocaine hydrochloride storage experiment using the zero flow reactor (ZFR). In the GC/MS chromatogram A, numerous peaks were observed. Many of the chromatographic peaks were saturated or beyond the linear dynamic range of the GC/MS instrument. The chromatographic peaks were due to compounds not structurally related to cocaine hydrochloride (i.e. methylene chloride). Interestingly enough, however, when the reactor was flushed with ultra zero air and not exposed to the air in the conditioning unit, a cleaner GC/MS chromatogram B was obtained.

Chromatogram A in Fig. 5 demonstrates that when the reactor was exposed to the environment of the conditioning unit, the contamination from the construction materials of the conditioning unit was severe. In the presence of the contaminants it was impossible to identify trace amounts of the cocaine hydrochloride degradation products.

Chromatogram B indicates that the contamination could have been avoided completely by using a more sterile environment which was achieved by closing the reactor system and by using conditioned clean air. In addition, the contamination was further minimized by replacing the materials that came in contact with the reactor with those that did not exhibit off-gassing. The humidification system was changed from an open source (as in an inorganic chemical saturated with water) to a closed source using a Nafion tubing. This provided better control of the relative humidity of the purge gas through the reactor. An additional improvement was made to the amount of exposed surface area of the cocaine hydrochloride sample. Instead of having cocaine hydrochloride sit in a pile on the bottom of a glass container, it was coated onto glass beads. This effectively increased the cocaine hydrochloride surface area exposed to the environmental conditions.

The sampling technique was changed from an external cryogenic loop to a sorbent tube because the moisture content of the reactor could plug up the GC column at subambient temperature.

Using the plug flow reactor it was observed that methyl benzoate was released when cocaine hydrochloride was exposed to ultra zero air even at very low humidities. Fig. 6 shows a GC/MS chromatogram of a plug flow reactor experiment. The two peaks represent deuterated and non-deuterated methyl benzoate. The deuterated methyl benzoate was used to quantify the methyl benzoate that was produced from the decomposition of cocaine hydrochloride. The important feature of this result is that the normal methyl benzoate was chromatographically separated from the deuterated methyl benzoate and the mass spectra of the two compounds are different (see Figs. 7 and 8) thus simplifying the quantitation of methyl benzoate from cocaine hydrochloride.

Fig. 9 shows a plot of methyl benzoate production over time from a cocaine hydrochloride storage study. Initially, the amount of methyl benzoate produced was very high but then the production decreased as the reaction proceeded. Table 1 summarizes the preliminary findings when cocaine hydrochloride was stored under different temperature/humidity conditions. The information in this table is congruent to that presented in Fig. 9. The effect of temperature and humidity is clearly demonstrated by the increase in the average production rate of methyl benzoate. This suggests that the decomposition reaction of cocaine hydrochloride is dependent on the moisture of the environment. The temperature effect indicates that this decomposition reaction is endothermic and can be promoted by a higher temperature.

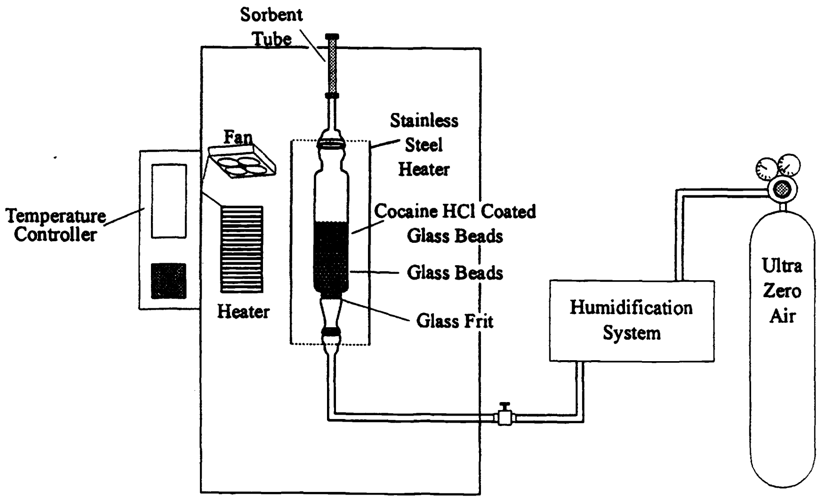

Fig. 3. Schematic diagram for the experimental setup to conduct the cocaine hydrochloride storage experiment using plug flow reactor (PFR)

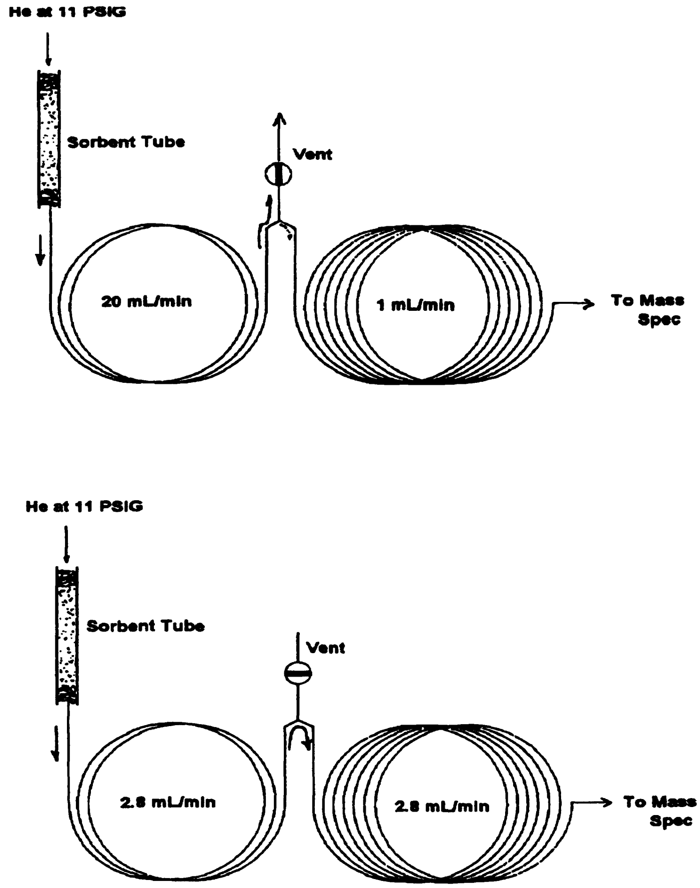

Fig. 4. Configuration of the split capillary column during thermal desorption (top) and GC/MS analysis (bottom)

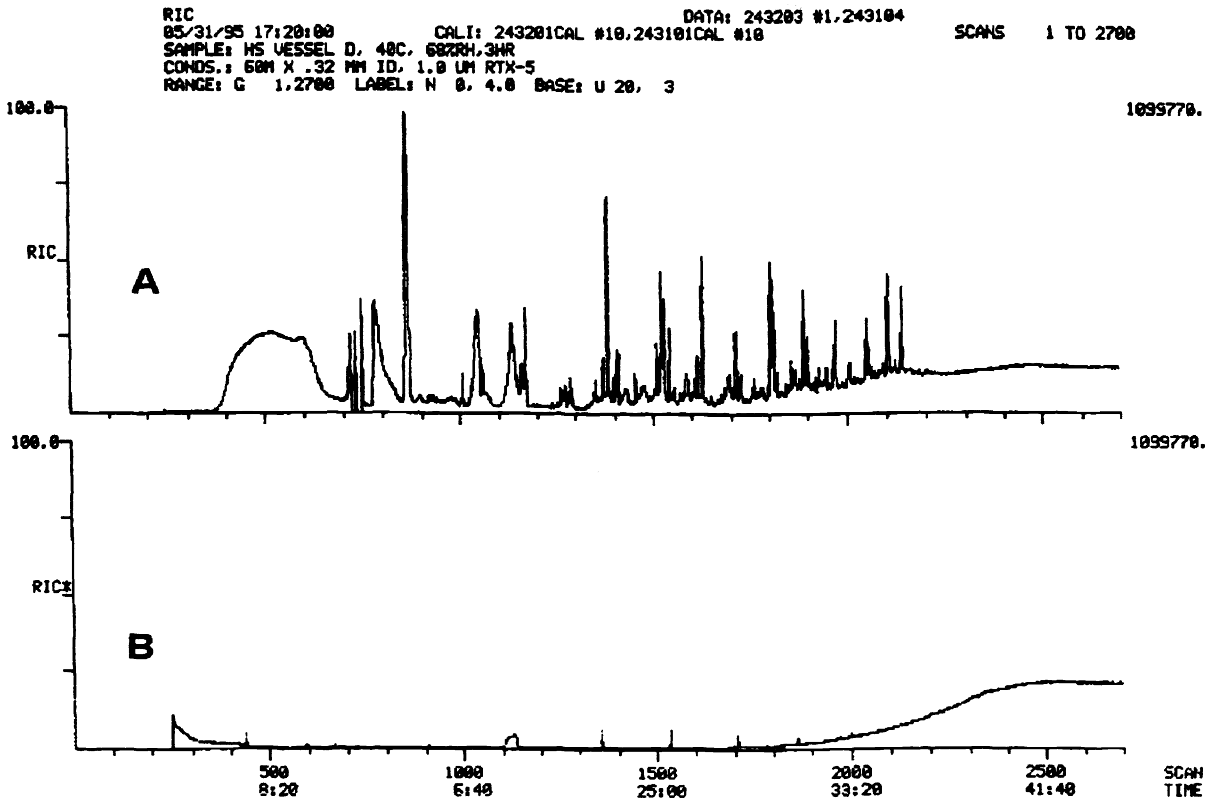

Fig. 5. GC/MS chromatogram for a storage experiment using a zero flow reactor

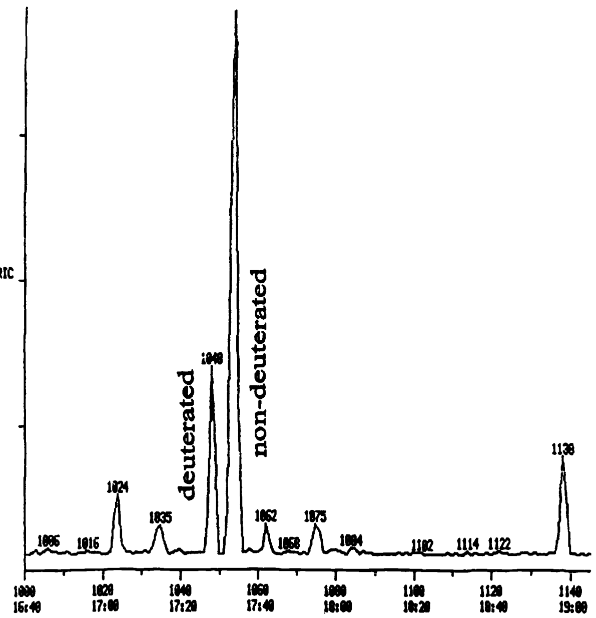

Fig. 6. GC/MS chromatogram of a cocaine hydrochloride degradation study using a PFR

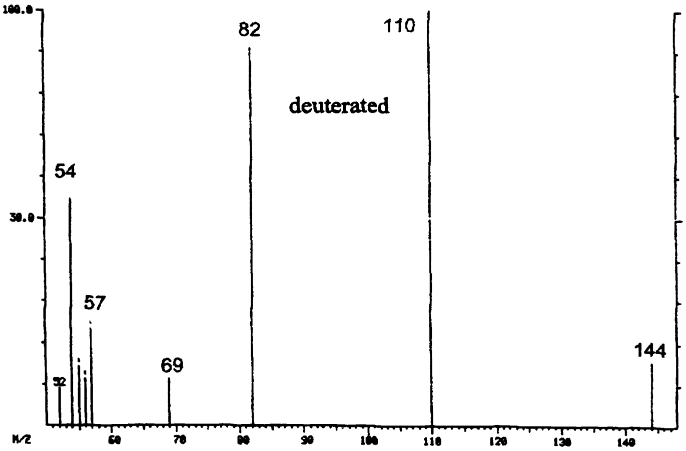

Fig. 7. Mass spectrum of deuterated methyl benzoate

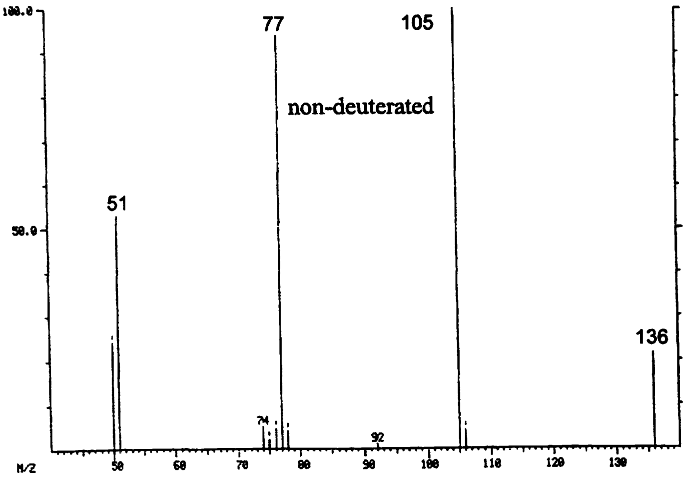

Fig. 8. Mass spectrum of non-deuterated methyl benzoate

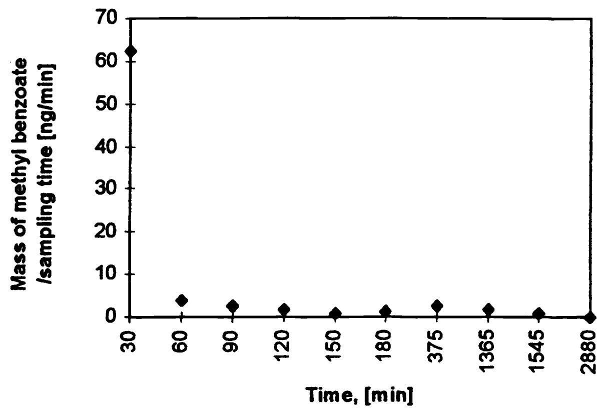

Fig. 9. Mass of methyl benzoate produced during a PFR trial as a function of time

Table 1. Methyl benzoate production using a plug flow reactor

PFR	1	2	3
Temperature	Ambient	40	40
Relative Humidity	2%	2%	81%
Sample Weight, g	0.300	0.318	0.316
Average Production Rate of Methyl Benzoate, ng/min	1.89	29	62
Percent Depletion of Cocaine HCl	0.000167	0.68	1.48

4. DISCUSSION

The observation of methyl benzoate as the product of the decomposition of cocaine hydrochloride is well supported by the results in Table 1 and Fig. 9. A significant increase was observed in the formation of methyl benzoate at higher humidities and temperatures. This indicates that the moisture in the conditioned ultra zero air was promoting the degradation of cocaine hydrochloride, as was the increase in temperature.

We infer that the formation of the methyl benzoate is via an acid catalyzed unimolecular trans-esterification reaction as shown in equation 1.

$$\text{Cocaine}\bullet\text{HCl} + H_2O \rightarrow \text{methyl benzoate} + \text{Product} \quad (1)$$

Here, the water acts as a solvent as shown in equation 2.

$$\text{Cocaine}\bullet\text{HCl} + H_2O \rightarrow \underset{\text{Cocainium ion}}{\text{CocaineH}^+(aq)} + Cl^-(aq) \quad (2)$$

The cocaine hydrochloride, like many salts such as ammonium chloride, dissolves in water to form an ionic solution. Since cocaine contains a strongly basic nitrogen, it is protonated to form a solvated cocainium ion. The cocainium ion undergoes unimolecular rearrangement to release methyl benzoate and another product. From the structure of cocaine, we suspect that the other product could be ecgonine.

5. CONCLUSION

From these results, we conclude that cocaine hydrochloride stored under environmental conditions ranging from ambient/dry to 40°C/81% RH, undergoes degradation to form methyl benzoate. Methyl benzoate is volatile, easily collected, analyzed and quantitated as demonstrated in this work. Most importantly, methyl benzoate is more readily detected than cocaine hydrochloride itself.

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7. ACKNOWLEDGMENT

This work was funded under contract number DAAD05-93-D-7021 through the Office of Special Technology (OST) (Mr. James Petrousky) under the auspices of the Counterdrug Technology Development Program Office (CDTDPO) (Mr. John J. Pennella). The authors would like to thank OST and CDTDPO for their continued support.

Attachment C9

Waggoner,L.P., Jonston, J.M., Williams, M., Jackson, J., Jones, M.H., BoussoM, T., and Petrousky, J.A., Canine Olfactory Sensitivity to Cocaine hydrochloride and Methy Benzoate, *Proceedings SPIE,* **2937:**19 (1996).

Canine olfactory sensitivity to cocaine hydrochloride and methyl benzoate

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ABSTRACT

Methyl benzoate is a consistent product of cocaine hydrochloride exposed to humid air. The detection responses of dogs trained to detect illicit cocaine hydrochloride may be controlled by vapor from cocaine, methyl benzoate, or other constituents of illicit cocaine. The present study addressed the following questions: (1) How capable are dogs of detecting methyl benzoate compared to cocaine hydrochloride? (2) When dogs are trained to detect methyl benzoate, do they respond to cocaine hydrochloride as being the same or different from methyl benzoate? These questions were investigated using random source dogs trained and tested under laboratory conditions. Odor stimuli were generated and delivered by a vapor generation systems, the outputs from which were characterized by thermal desorption GC/MS. One group of dogs was trained to discriminate pharmaceutical grade and illicit cocaine hydrochloride from clean air and tested using a two lever procedure to determine their sensitivity to these substances. A second group of dogs was trained to discriminate between methyl benzoate and clean air and tested for their sensitivity to the substance . The dogs in this second group were then tested using a three lever procedure to determine whether they responded to cocaine hydrochloride as the same or different from methyl benzoate.

1. INTRODUCTION

The dog's olfactory detection capabilities rival or surpass that of analytical instruments, and the dog-handler detection team remains the most effective technology available to law enforcement for the detection of narcotics[1]. Despite the proven usefulness of the dog-handler team, scientific investigation of canine detection capabilities for substances of interest to the law enforcement community has been limited. A 1991 report by the U.S. Congress Office of Technology Assessment concluded that a serious weakness of using canines for detection purposes is that their detection capabilities have not been quantified[1]. The following laboratory study of dogs' detection of cocaine hydrochloride and its degradation product methyl benzoate were conducted as part of the ongoing efforts of Auburn University's Institute for Biological Detection Systems to enhance canine detection technology.

Complete characterization of canine olfactory detection of a substance requires investigation of two aspects of detection. First, the extent and nature of the dog's sensitivity to a substance must be examined. This requires assessment of the dog's response to a range of substance concentrations in order to determine the lower detection limit, or threshold, as well as to characterize supra-threshold performance.

Second, the components of the substance on which that sensitivity depends (i.e., the detection odor signature) must also be determined[2]. Substances targeted for detection usually involve multiple chemical components. Such is the case of illicit cocaine, which contains many constituents besides cocaine hydrochloride, whether as natural byproducts or as contaminants from processing or packaging [3]. The method for determining the detection odor signature involves training a dog to respond differentially to clean air, the target odor, and non-target odors[2]. The dog's reactions to constituent compounds can then be assessed individually or in particular combinations. This was not the present challenge, however. Instead, a confirmatory method of evaluating the role of a specified constituent compound was used that

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involves determining whether a dog is using that constituent by training it to detect the constituent and then assessing its reaction to the whole substance.

The following studies sought to determine canine sensitivity to cocaine hydrochloride and methyl benzoate, as well as to assess the role of methyl benzoate in canine detection of cocaine hydrochloride. Methyl benzoate is an consistently abundant constituent found in illicit cocaine samples. There are three possible sources of methyl benzoate in illicit cocaine. It may be present as a naturally occurring compound co-extracted with cocaine from coca leaves, as a decomposition byproduct resulting from the use of excessive hydrochloric acid in isolating cocaine hydrochloride, and as a product of the hydrolysis of cocaine[3]. The hydrolysis of cocaine is thought to contribute the greatest amount of methyl benzoate to the vapor from illicit cocaine samples[4]. Although benzoic and acetic acid are also abundant constituents of illicit cocaine vapor, methyl benzoate was chosen for study because of anecdotal reports that it smells similar to some illicit cocaine samples and has sometimes been used to train dogs to detect cocaine.

In service of these objectives, this study had three components. (1) One group of dogs was trained to detect first pure cocaine hydrochloride and then an illicit sample of cocaine hydrochloride. The concentration of each type of cocaine was then systematically varied to obtain a measure of detection sensitivity. (2) A second group of dogs was trained to detect methyl benzoate, the concentration of which was then varied to obtain a measure of detection sensitivity. (3) The dogs trained on methyl benzoate were also taught to discriminate between methyl benzoate and any compound that does not smell like the illicit cocaine hydrochloride sample. Their reactions to illicit cocaine hydrochloride were then tested to determine if it smelled like methyl benzoate.

2. METHODS

2.1 Subjects

Thirteen medium to large size, intact and neutered, male and female adult canines of normal health and physicality were used in these studies. These random source dogs were acquired by the Department of Lab Animal Health of Auburn University's College of Veterinary Medicine. Dogs were maintained at between 85% to 95% of their normal weight, as determined by a period of free feeding.

2.2 Apparatus and materials

2.2.1 Experimental chamber

Dogs were trained and tested in sound-attenuated experimental chambers (97 cm x 72 cm x 100 cm) (Fig. 1.). Centered on the front wall was an aluminum interface panel (60 cm x 60 cm). The interface panel contained either 2 or 3 stainless steel response levers (8 cm x 8 cm) located 54 cm above the floor, sound generating devices, and a 9 cm diameter opening that allowed the dog access to a 1 liter glass scent chamber into which odor stimuli were presented. A bowl was attached to the floor below the interface panel to receive food pellets (Hills, Canine Growth Formula) delivered by an automated feeder (Gerbrands) attached to the back of the chamber. A photo beam unit (Radio Shack) that detected muzzle insertion into the scent chamber was mounted on the back of the interface panel. General illumination was provided by an incandescent bulb. Ventilation was provided by a small fan pulling room air into the chamber, and vacuum lines attached to 4 ports about the perimeter of the scent chamber provided exhaust.

2.2.2 Vapor generation

2.2.2.1 Single source olfactometer

For determining canine sensitivity, a serial air diluting vapor generator or olfactometer was used. This device delivered to the scent chamber for each odor trial samples of vapor from odor source material

diluted by clean air supplied by purge gas generators (Peak Scientific). The relative humidity of the air supplied by the purge gas generators was < 1 %. On non-odor or blank trials, the device delivered clean air only. The multiple channel design of the instrument allowed the delivery of two concentrations of odor vapor within a session. The performance of the instrument was assessed by thermal desorption GC/MS. Details of the design and performance of the instrument have been described elsewhere[5].

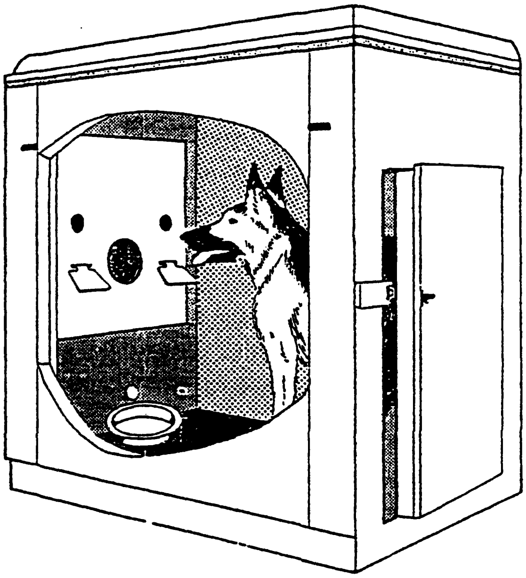

Figure 1. Drawing of experimental chamber

2.2.2.2 Multiple source olfactometer

For assessing the role of methyl benzoate in canine detection of cocaine hydrochloride, a multiple source vapor generation device or olfactometer was used. This device delivered to the scent chamber on target trials a single dilution of a vapor from the target substance. On non-target trials, the device delivered a single dilution of one of two non-target substances and on non-odor or blank trials, delivered clean air. On probe trials the device delivered a single dilution of the test substance. The performance of the instrument was assessed by thermal desorption GC/MS. The materials and components of this instrument are identical to those of the single source olfactometer described in detail by Hartell et al.[5]

2.2.3 Control equipment

All experimental events and data acquisition were controlled through interface components (Coulbourn) by a PDP 1173 microomputer (Digital Equipment) running Micro RSX (Digital Equipment) and Sked-11 software (State Systems). Data processing and preparation of graphs was accomplished on a PC with AXUM Technical Graphics software (Math Soft).

2.2.4 Odor Sources

Methyl benzoate and pharmaceutical cocaine (>99% pure) as well as the non-target odor sources (amyl-butyrate, allyl sulfide, amyl butyrate, dimethyl thiazole, and alpha-ionone) were obtained from Sigma Chemical Company. Illicit cocaine was obtained from the Alabama Bureau of Investigation.

2.3 Procedures

2.3.1 Olfactory sensitivity

Dogs were trained for olfactory testing using a modified backward chaining procedure[6]. This involved training the last response in a chain first and adding response links in backward order one at a time until the first response in the chain was learned. This chain included: 1) inserting muzzle into scent chamber in the presence of a beeping tone until the constant tone was presented (2 s), 2) pressing the left lever on trials when clean air was present in the scent chamber and the right lever on trials when odor was present in the scent chamber, and 3) eating food when presented, and 4) waiting for the next trial (22s). Lever press and muzzle insertion responses were trained using shaping and fading procedures[7]. Shaping, training, and maintenance of the complete performance were accomplished by the presentation of food for correct responses and blackouts of chamber illumination (15 s) for incorrect responses.

Before testing began, the proportion of correct trials followed by food was decreased from 1.0 to 0.725. This aided maintenance of responding[7] and allowed presentation of low concentrations as probe trials, on which responses resulted in neither food presentation nor blackouts. Lower concentrations of odor were presented as probe trials in order to maintain the dogs' accuracy in discriminating odor from clean air[8]. In sessions involving low concentration probe trials, a higher concentration was presented on the remaining odor trials.

Testing began when a dog's accuracy of discriminating clean air from varied concentrations of the target odor was consistently high. Testing involved presenting different concentrations of odor in a quasi-random order. Equal proportions of clean air and odor trials were programmed to occur in quasi-random order in each session. In some test sessions, a single concentration of odor was presented. As testing progressed and lower concentrations that engendered accuracy near 70% were evaluated, test sessions consisted of probe trials of lower concentrations and higher concentrations for remaining trials. Sessions lasted approximately 55 minutes, and the time between trials was 22 s. The time between trials allowed the dog's nose to recover from the previous trial and the vapor generator to prepare for the next scheduled sample [9].

In summary, a typical session consisted of about 65 clean air trials and 65 odor trials or, if the session included probe trials, 53 higher concentration odor trials and 12 probe trails. The relatively low proportion of probe trials was required so that the percentage of left and right lever responses resulting in food presentation did not become too disparate when accuracy of detecting the probed concentration was high. Testing ended when at least 3 sessions and 20 trials were obtained for each concentration (Table 1) necessary to describe the dog's sensitivity to the odor, although the total number of sessions and trials per concentration often exceeded 100 trials. Seven dogs were trained and tested on vapor from methyl benzoate. The other dogs were trained and tested on vapor from pharmaceutical (N = 7) and illicit cocaine hydrochloride (N=5).

Table 1. Approximate concentrations of methyl benzoate vapor from methyl benzoate and illicit cocaine delivered in testing sessions. Each subject was not presented with every concentration

Source	*Approximate Concentrations of Methyl Benzoate (ppb)*											
Methyl Benzoate	960	580	320	190	100	58	30	16	10	6	3	2
Illicit Cocaine	0.80	0.62	0.43	0.24	0.14	0.08	0.05	0.25	0.01	0.007	0.004	0.002

2.3.2 Determination of the role of methyl benzoate in the detection of cocaine

Five of the dogs trained and tested with methyl benzoate in the sensitivity determination portion of this study were further trained to press a middle lever on trials when vapor from non-target compounds (i.e., compounds other than methyl benzoate or the compounds found in illicit cocaine) were presented to the scent chamber. This discrimination was a key component of this procedure and provided the means for assessing the role of methyl benzoate in the detection of cocaine. First, a discrimination between the initial non-target and the other two samples (clean air and methyl benzoate) was trained. When

discrimination between the three samples was achieved, the dog learned to discriminate a second non-target odor from clean air and methyl benzoate. Subsequently, a third and fourth non-target was introduced in a similar manner. Training was considered complete when middle lever responding was predominant in the presence of novel non-target odors without training. Such responding indicated that middle lever responding had generalized to all odors other than methyl benzoate. For all dogs, generalized responding to the middle lever was observed upon presentation of the third and fourth non-target odor.

Test sessions consisted of clean air, non-target A, non-target B, and target odor (methyl benzoate) trials as well as probe trials with vapor from illicit cocaine hydrochloride. The illicit cocaine vapor was presented as probes to prevent influencing the dog's reactions to illicit cocaine vapor with differential consequences (food presentation or black-outs) [9]. Because of a training history that included high concentrations of the methyl benzoate and an inability to produce higher concentrations of the probe odor, the concentration of the target and non-target samples were systematically lowered before testing began. Equal proportions of clean air, target, and non-target trials in quasi-random order were programmed to occur in each session. Sessions lasted 45 minutes with 18 s elapsing between trials resulting in a typical session having 30 clean air, non-targets, and target trials each and five to ten cocaine probe trials. Testing was considered complete when enough probe trials had been run to describe the pattern of a dog's responding when presented with vapor from illicit cocaine hydrochloride.

3. RESULTS

3.1 Canine sensitivity to pharmaceutical cocaine HCl, illicit cocaine HCl, and methyl benzoate

The measures used to assess sensitivity to different concentrations of odor stimuli were percentage of hits (i.e., the percentage of odor trials on which a dog pressed the target lever), and the overall percentage of false positives (i.e., the proportion of air trials on which a dog pressed the target lever). Both measures are required to describe sensitivity in order to show the control engendered by the presence or absence of the odor[8]. Because more than one concentration of a target odor was presented in probe sessions, the percentage of false positive responses could not be determined for each concentration. Therefore, the overall false positive percentages across sessions are displayed in graphs. Data were excluded from analysis when the false positive percentage was greater than 22 % (except for comparisons between pharmaceutical and illicit cocaine) to further assure that the data reported reflected good sensitivity to the target odor.

While training dogs to detect pharmaceutical cocaine, it became apparent they could detect only the highest concentrations of this vapor that could be generated. This can be seen by comparing pharmaceutical and illicit cocaine detection across the first four odor dilution levels in Figure 2. This figure shows detection performance in relation to dilution level rather than concentration because pharmaceutical cocaine vapor was indistinguishable from clean air by chemical analysis as delivered via the vapor generation device. Nonetheless, it is clear that some of the dogs did discriminate pharmaceutical cocaine from clean air, though with considerably less accuracy than they discriminated illicit cocaine vapor from clean air. The accuracy for detecting pharmaceutical cocaine fell below 50% for some of the dogs at the 150 ccm level, whereas their accuracy in detecting the illicit cocaine remained relatively high. Figure 2 also shows that higher false positive percentages (bottom right) occurred with pharmaceutical cocaine. Two of the seven dogs tested on pharmaceutical cocaine, which was run first, had to be removed from the study, leaving five dogs to be tested on illicit cocaine.

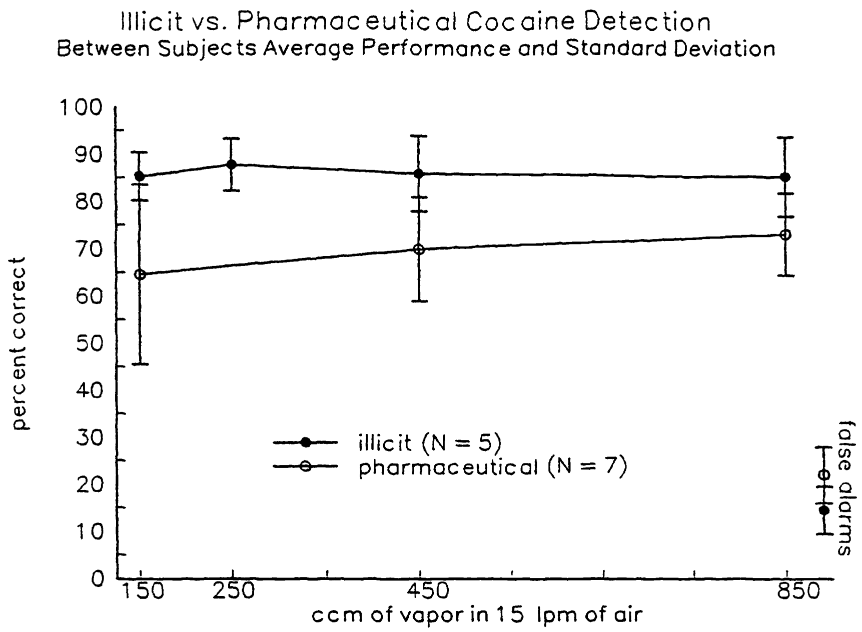

Figure 2. Comparison of canine detection performance for pharmaceutical and illicit cocaine.

The olfactory sensitivity functions for illicit cocaine are presented in Figure 3. Individual dog's sensitivity functions in terms of hit percentages are shown in relation to concentrations of methyl benzoate in the vapor from illicit cocaine. Methyl benzoate was used as the tracer constituent for the concentration of the vapor from cocaine because 1) cocaine was not detected in the vapor by GC/MS, 2) methyl benzoate was the most abundant and consistent constituent of the vapor, and 3) methyl benzoate was the constituent of greatest interest in this study. A lowess (locally weighted scatter plot smoothing) smoothing algorithm[10] and cubic spline smoothing were used to provide a nonparametric fitted line allowing estimation of the absolute threshold, a statistical concept equivalent to the concentration at which each dog is accurate on 50% of odor trials[8]. Threshold estimations, indicated by the vertical dotted lines, ranged from a low of about 0.02 to a high of about 0.04 parts per billion of methyl benzoate. The mean false positive percentage across concentrations for each dog is also displayed (bottom right). The average false positive percentage across dogs was 9.6. Four of the dogs had similar sensitivity functions with hits ranging between 80% and 90% at concentrations above 0.1 ppb and falling rapidly below 0.05 ppb. Dog 7107's hit rate declined more rapidly than that of other dogs and resulted in the highest estimated threshold (0.037 ppb) as well as false positive percentage (12%) of all dogs.

Canine olfactory sensitivity functions for methyl benzoate are displayed in Figure 4. Thresholds estimated from the lowess smoothing algorithm (vertical dotted lines) applied to each dog's data range from 5 ppb to 27 ppb, and the average false positive percentage (bottom right) across dogs was 6.33. Similar functions were obtained for all dogs although dog 6251 had a higher hit percentage at lower concentrations and dog 6882 was less accurate than the other dogs. With the exception of dog 6882, hits at concentrations above 50 ppb were above 90%. Below 50 ppb, variability in accuracy between dogs increased and the hit percentages declined rapidly.

Canine Detection of Illicit Cocaine HCl

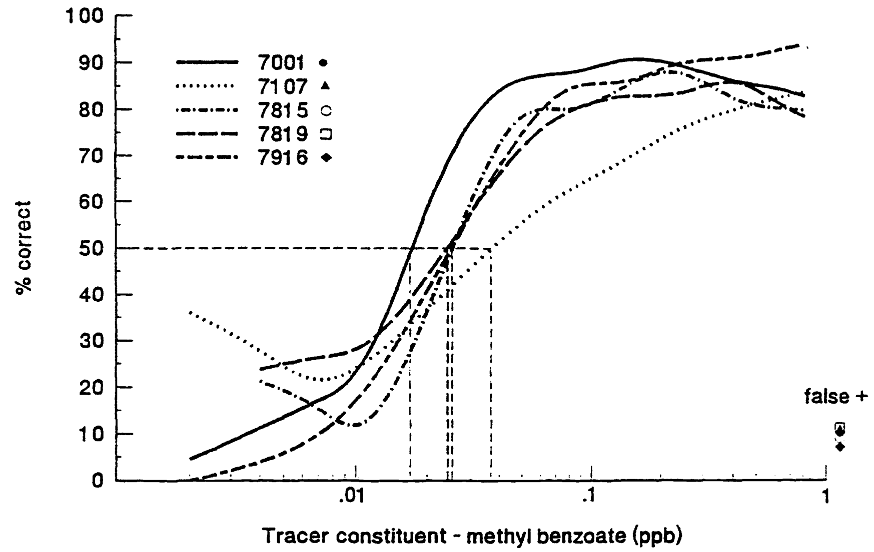

Figure 3. Canine sensitivity functions and threshold estimations for illicit cocaine vapor

Canine Detection of Methyl Benzoate

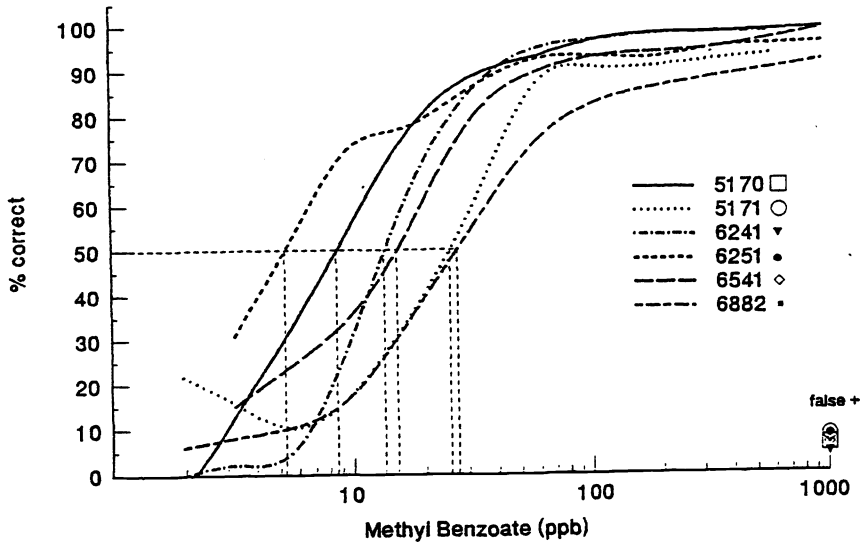

Figure 4. Canine sensitivity functions and threshold estimations for methyl benzoate vapor

3.2 The role of methyl benzoate in the detection of illicit cocaine hydrochloride

The responses of dogs trained to discriminate methyl benzoate from other odors in the three lever procedure are described by the percentage of responding on the clean air (left), non-target (middle) and methyl benzoate (right) levers in Figure 5. The aggregate percentages across correct detections on clean

air trials (88.2%), non-target trials (77.16%), and methyl benzoate (target lever) trials (78%) during non-probe trials are shown on the left of the figure. The percentage of air, non-target, and target lever responses for each dog on illicit cocaine probe trials are shown on the right. The responses of dogs 5170 and 6241 were distributed almost evenly across the three levers. For dogs 6251 and 6541, clean air responses predominated. Dog 6882 had the highest percentage of methyl benzoate responses and the lowest percentage of clean air responses among the dogs.

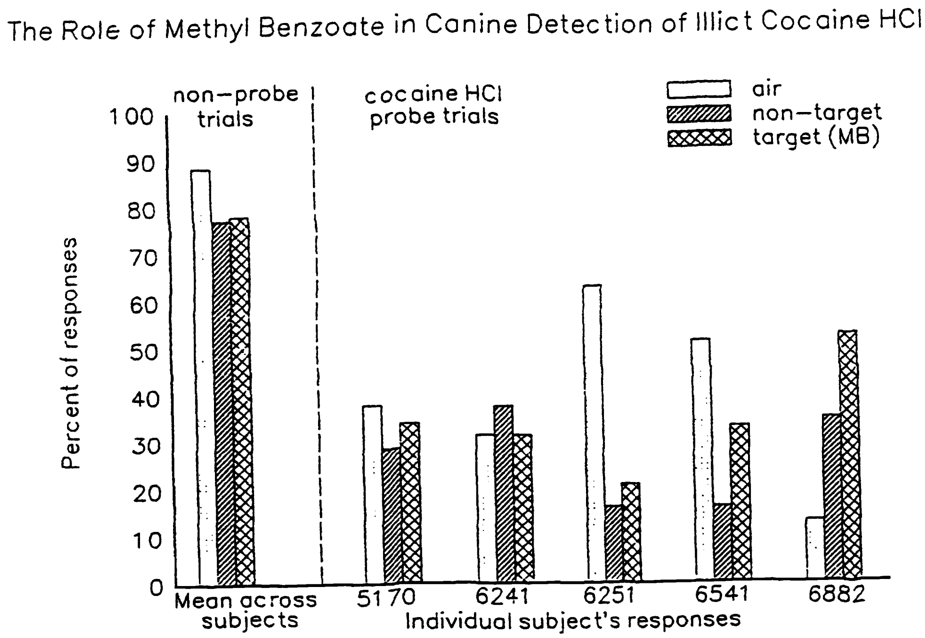

Figure 5. Percentage of air, non-target and target lever responding averaged across dogs for non-probe trials and of individual dogs for cocaine probe trials.

4. DISCUSSION

4.1 Canine sensitivity to pharmaceutical coccaine HCl, illicit cocaine HCl, and methyl benzoate

Comparing canine detection performance for pharmaceutical and illicit cocaine HCl revealed that, under the conditions of vapor generation in this experiment, dogs are more sensitive to vapor from illicit than pharmaceutical cocaine. This is not surprising given that the pharmaceutical cocaine was more than 99% pure and the illicit sample was approximately 92% pure. Furthermore, the clean air used for dilution was less than 1% relative humidity, which would minimize the amount of methyl benzoate produced from either sample by the vapor generation system[4]. As a result, constituents from the illicit cocaine sample were detectable at lower dilution levels by GC/MS analyses, whereas nothing at all was detected in the vapor from pharmaceutical cocaine at those same dilution levels as delivered by the vapor generation system. Cocaine HCl was detected by GC/MS in vapor from both sources only when an undiluted sample was analyzed. This evidence suggests that when dogs are trained to detect cocaine in the field, their discriminations probably depend on one or more constituents in the vapor sample in addition to cocaine HCl.

The sensitivity functions for illicit cocaine reveal that dogs are capable of detecting vapor from illicit cocaine at concentrations in which the abundance of methyl benzoate was less than 0.1 ppb. The low false

positive percentages indicate that control over responding by the presence and absence of vapor from illicit cocaine was quite good across the range of concentrations presented (Table 1). The dogs' performances at the lowest dilution levels were somewhat less accurate than those obtained at the lowest dilution levels delivered for methyl benzoate. Otherwise, the shape of the functions obtained were similar to those obtained for methyl benzoate, and consistent with sensitivity functions for a variety of sense modalities across many species [11].

The average sensitivity threshold for methyl benzoate vapor was 16 ppb compared to 0.03 ppb for illicit cocaine vapor (as measured by methyl benzoate as a tracer constituent). (It is possible that sensitivity to methyl benzoate might be lowered somewhat by extended exposure to discrimination training.) This means that the highest methyl benzoate concentration in the illicit cocaine vapor was lower than the dogs' average threshold for methyl benzoate vapor. In other words, the dogs were not apparently using methyl benzoate when detecting illicit cocaine under these laboratory conditions. This suggests that compounds in cocaine other than methyl benzoate may be important in how dogs recognize cocaine.

4.2 The role of methyl benzoate in canine detection of illicit cocaine hydrochloride

If methyl benzoate is the constituent of vapor from cocaine HCl that controls canine detection of cocaine, then dogs trained to discriminate methyl benzoate from other odors and clean air would be expected to respond to cocaine HCl vapor samples as if they were methyl benzoate. As can be seen in Figure 5, the percentage of responses on the methyl benzoate (target) lever on cocaine probe trials did not approach the average non-probe performance on methyl benzoate trials for any dog. Dog 6882 was the only one that responded to illicit cocaine probes as most often smelling like methyl benzoate (52.6%). The responses of two other dogs (5170 and 6241) were almost equally divided across the three levers, indicating they detected some odor (target or non-target) on about two thirds of the trials but showed no tendency to report that the illicit cocaine probes smelled more like methyl benzoate than another odor. Dogs 6251 and 6541 responded to the clean air lever on most cocaine probe trials, though when 6541 did detect an odor, it responded mostly to the methyl benzoate (target) lever. Perhaps the most important observations from tests of these methyl benzoate trained dog's reactions to cocaine probes (Fig. 5) are that (1) when three of the dogs (5170, 6241, & 6251) detected some odor on cocaine probe trials, their responses were about equally divided between the non-target and target (methyl benzoate) levers and (2) when the other two dogs (6541 & 6882) detected some odor, they most often responded to the methyl benzoate (target) lever on cocaine probes, indicating that illicit cocaine vapor smelled like the vapor presented on methyl benzoate trials.

Although these results do not indicate that methyl benzoate is the detection odor signature for illicit cocaine, they do suggest that methyl benzoate may be one of the constituents of the illicit cocaine odor signature for dogs. The odor signature refers to the constituent or multiple constituents of a substance that controls the olfactory detection responses of a dog [2]. Constituents that are abundant in the vapor of a substance are likely candidates for a detection signature. But abundance may not be the sole predictor of an odor signature. In the case of cocaine, the results of this study indicate that a combination of methyl benzoate plus other constituents (e.g. benzoic and acetic acid or ecogine[4]) may be required to define the odor signature.

These results should not be considered a definitive evaluation of the role of methyl benzoate in canine detection of illicit cocaine. Ideally, the concentration of methyl benzoate presented in target odor trials should be adjusted to match the concentration of methyl benzoate in the vapor from cocaine presented in probe trials. With the vapor generation system used in this study, however, a limitation was encountered in reducing the concentration of vapor generated from methyl benzoate to the low levels produced with the cocaine. The concentration of methyl benzoate delivered on target trials was approximately 15 ppb and the approximate concentration of methyl benzoate in the vapor from the illicit cocaine was 0.1 ppb. A somewhat clearer picture of the role of methyl benzoate in cocaine detection might have been obtained had the concentrations been more closely matched. Resolution of this issue can best be approached by

determining the detection odor signature for cocaine, which would clarify the possible role of other constituent compounds in illicit cocaine.

4.3 General Discussion

Canines are capable of detecting low levels of cocaine hydrochloride and methyl benzoate. In the present study, the detection capabilities of the dog surpassed the detection limits of the analytical instruments used in characterizing the output of the vapor generation devices. Although questions remain concerning the difference between the vapor detection thresholds for illicit cocaine and methyl benzoate, it is clear that the canine is a viable detector of both substances.

Developing effective detection training aids requires consideration of the canine's sensitivity for a substance, as well as its detection odor signature for that substance. Although the role of methyl benzoate in the detection of cocaine is important, it may not constitute the full detection odor signature for illicit cocaine. The present results offer a caution against predicting detection odor signatures or selecting training aids based only on the relative abundance of the constituents of a substance.

Of course, there are differences in the laboratory setting of this study and the conditions under which dogs work in the field. The humidity of the air used in generating vapor was such a variable. Under field conditions, the level of methyl benzoate produced by the degradation of cocaine would be much higher than was obtained in the laboratory because of the higher humidity levels of non-laboratory environments, perhaps resulting enhanced detection performance. In the present study, humidity levels were held constant and were quite low, which allowed a more consistent level of methyl benzoate production from illicit cocaine than could be achieved if humidity level was allowed to vary. This caveat might suggest that had test conditions used humidity levels typical of field conditions the higher levels of methyl benzoate in illicit cocaine vapor samples might have led dogs to respond to cocaine probes as smelling like methyl benzoate. However, recall that it was also determined that the threshold for illicit cocaine vapor was lower than for methyl benzoate, indicating that dogs can detect illicit cocaine using constituents other than methyl benzoate. Future studies should examine the effects of humidity levels on the detection of cocaine.

The goals of laboratory studies such as these are to characterize the extent and mechanisms of olfactory detection to provide a foundation for the development of enhanced canine detection technology. In doing so, such studies also help maintain the well deserved credibility of the dog as a detection technology competitive with or superior to other detection technologies. The present attempts to determine canine sensitivity to cocaine HCl and methyl benzoate, as well as determine the role of methyl benzoate in cocaine detection, represent the ongoing efforts of the Institute for Biological System to better understand the impressive detection performance of dogs.

5. ACKNOWLEDGMENTS

This work was supported and funded by the Office of Special Technology, U. S. Department of the Navy (DAAD05-93-D07021 & DAAD05-96-D7019). We gratefully acknowledge the assistance of Battelle Memorial Institute, the Federal Aviation Administration and the Treasury Department. Bart Bedford provided invaluable technical support for this project.

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Attachment C10

Furton, F.G., Hsu,Y., Luo, T., Alvarez, N., and Lagos, P., Novel Sample Preparation methods and Field Testing procedures used to Determine the Chemical Basis of Cocaine detection by Canines, *Proceedings SPIE*, **2941** (1997).

Novel sample preparation methods and field testing procedures used to determine the chemical basis of cocaine detection by canines

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ABSTRACT

The use of canines to signal money associated with drug trafficking is a major point of contention among dog handlers, forensic scientists, and the legal community particularly in light of recent reports that a significant amount of money in circulation is contaminated with detectable amounts of cocaine. The questions raised include: What exactly are the dog alerting to? How selective are the dogs? How sensitive are the dogs? How reliable are the dogs? Tests with various volatile cocaine by-products confirm that the dominant chemical in cocaine odor is methyl benzoate. Field tests on fifteen different drug detector dogs with varying breeds, ages and training regimes show a consistent threshold level of 1 μg of methyl benzoate spiked along with cocaine on US currency required to initiate an alert. The majority of the canines did not alert to pharmaceutical grade cocaine even at levels as high as 1 g. Methyl benzoate is shown to evaporate rapidly from individual bills and is a function of the available surface area for wrapped currency. The canines tested were remarkably selective and reliable even under varying test conditions and using different delivery devices.

Keywords: canine detection, cocaine, methyl benzoate, currency, contamination.

1. INTRODUCTION

The purpose of the proposed work is to confirm the identity, quantity and significance of chemical markers which trigger a detector dog to alert to cocaine. The use of canines in drug detection has long been recognized and accepted in courts of law. However, the use of these same drug detector dogs to indicate money associated with drug trafficking has recently become is a major point of contention. This issue has come to a head in light of recent reports suggesting that all money in circulation is tainted with trace levels of drugs, including cocaine [1]. These reports have resulted in contaminated money theories purporting that due to this widespread contamination, any person carrying currency could potentially initiate a drug dog alert. The legal significance of this theory ranges from reducing the probative value of drug dog alerts to the complete elimination of drug dog utility if, indeed, canines can alert to any sum of currency.

The urgent need for better scientific information and detector dog standards is clearly evident from the current attacks on drug detector dog alerts using so-called contaminated money theories. This contaminated money theory was recently relied upon by the Ninth U.S. Circuit Court of Appeals which upheld the dismissal of a forfeiture case stating that "The government's failure to demonstrate by some credible evidence the probability that Alexander's money was in fact drug-related, coupled with the uncontroverted evidence that greater than seventy-five percent of all circulated money in Los Angeles is contaminated with drug residue, distinguish this case from our previous cases" [2].

Reports cited in the above court's decision include a June 15, 1992, newspaper article from the Orlando Sentinel [3] stating that six of the eight [bills] from so-called non-users showed detectable amounts of cocaine that were "well within the range of a drug dog's detection ability" and testimony of a Dr. James Woodford that ninety percent of all cash in the United States contains sufficient quantities of cocaine to alert a narcotics detection dog. These conclusions are alarming in light of the fact that there are no definitive peer-reviewed studies demonstrating the "range of a drug dog's detection capability" to cocaine nor are there any statistically significant determinations of the degree and extent of cocaine contamination on U.S. currency. Although the limited above mentioned studies indicate that there is widespread contamination of U.S. currency by detectable levels of cocaine, the actual levels and significance to canine detection have not been established with any degree of scientific certainty.

There are at least five major issues which need to be addressed and illustrate the current lack of scientific validity of the contaminated money theory. Firstly, to be statistically meaningful, any study attempting to determine the extent and quantitative level of cocaine contamination in a particular geographic area must obtain a sufficient number of different denomination bills ensuring that a representative sample of currency in general circulation is obtained. The limited reports quoted to date rely on tiny sample sizes chaotically sampled from specific sites and from various geographical regions [1] and cannot be extrapolated to represent the more than $400 billion in U.S. paper currency in circulation at any given time. Secondly, since the average lifetime of U.S. paper currency is relatively short, studies should be carried out on a regular basis accounting for the constant turnover of paper bills and therefore the variability of any contamination levels as a function of time. Thirdly, since it is clear that canines do not alert to a single molecule of a chemical but, rather, to significant concentrations of the chemical, additional studies are needed to confirm the threshold, range and specificity of canines to detect the volatile chemicals associated with cocaine before any general conclusions can be reached. A fourth major issue is that quantitative levels of volatile chemicals associated with cocaine and proven to elicit an alert by drug detection canines, such as methyl benzoate, have never been reported on paper currency. And finally, properly trained drug detector dogs have been shown repeatedly not to alert to circulated currency [4]. This issue can be resolved by proper training and documentation of the drug detector dog.

To the author's knowledge, the only research papers published on cocaine contamination which have addressed currency flow and systematically sampled hundreds of bills of each different denomination all from a specific area did not find substantial levels of cocaine contamination on the surface of circulated currency. One study on cocaine contamination on Canadian currency in Saskatchewan found background cocaine levels on 2100 bills of circulated money of less than 10 nanograms per note and currency seized in drug investigations with cocaine levels 50 to over 1000 times the background levels [5]. In a study of surface cocaine contamination of circulated money, 2000 bills were tested confirming that cocaine is present on money in general circulation, but not in sufficient quantity to be easily removed except by solvent washing. However, paper currency contaminated by counting the money with micrograms of cocaine on the fingertips did yield detectable quantities of cocaine by a shaking method [6].

2. RESULTS AND DISCUSSION

Some likely decomposition pathways for cocaine are shown in Figure 1. We have also found that methyl benzoate readily forms in cocaine formulations over a period of time when exposed to solvents such as methanol but does not spontaneously form to any appreciable extent in pharmaceutical grade cocaine as seen in Table 1.

TABLE 1. Percent methyl benzoate formed in cocaine specimens as a function of time.

Specimen	initial	1 week	2 weeks	3 weeks
10,000 ppm cocaine base in methanol	0.034%	3.6%	6.2%	7.3%
10,000 ppm cocaine HCl in methanol	0.0048%	0.0091%	0.019%	-
10,000 ppm cocaine base in chloroform	0.00007%	0.00013%	0.00015%	-
10,000 ppm cocaine HCl in chloroform	0.00049%	0.00045%	0.00059%	0.00081%
Solid pharmaceutical grade cocaine base	0.00013%	0.00015%	0.00010%	0.00014%
Solid pharmaceutical grade cocaine HCl	0.00069%	0.00068%	0.00061%	0.00053%

The dominant decomposition product upon thermal decomposition or hydrolysis for pharmaceutical grade cocaine is benzoaic acid as seen in Figure 2, showing the percent benzoic acid formed upon injection into a GC injection port at different temperatures. Athough appreciable amounts of benzoic acid were produced when cocaine was exposed to humid conditions or heated above 200°C, no appreciable increase in methylbenzoate concentration was observed. Whereas the parent cocaine molecule is non-volatile and can remain of currency for long periods of time, the volatile decomposition products such as methyl benzoate dissipate quickly as seen in Figure 3. We have performed tests on fifteen different drug detector dogs with varying breeds, ages and training regimes. U.S. paper currency was spiked with successively increasing amounts of cocaine and volatile cocaine by-products, including methyl benzoate , benzoic acid ecgonine, ecgonine methyl ester, trans-cinnamic acid, methyl trans-cinnamate and ethylbenzoate. 9 inch round galvanized steel box containing the spiked currency were placed in a test room with carefully monitored humidity, temperature, air flow, etc. as seen in Figure 4. The hand hole on one side of each cardboard box or 6 small drilled holes in the metal boxes were opened to allow each dog to sniff the atmosphere generated. The dog handlers did not know the contents of the boxes and were simply instructed to have their dogs sweep the test room for controlled substances. Our results indicate that drug detector dogs alert to the common volatile cocaine by-product, methyl benzoate rather than to the cocaine itself. None of the dogs tested alerted to by-products other than methyl benzoate and the majority did not alert to synthetic "pure" cocaine even at the highest levels tested of 1 g as seen in Table 2. The "pure" cocaine standards we obtained from commercial sources were found by GC/MS to be contaminated with small amounts of detectable impurities including methyl benzoate.

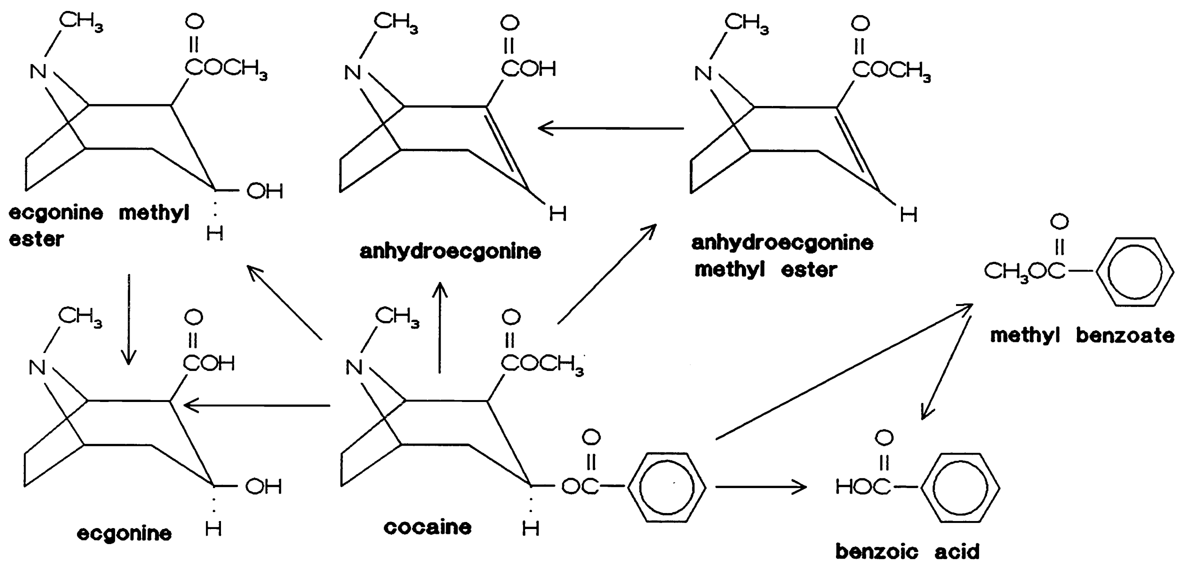
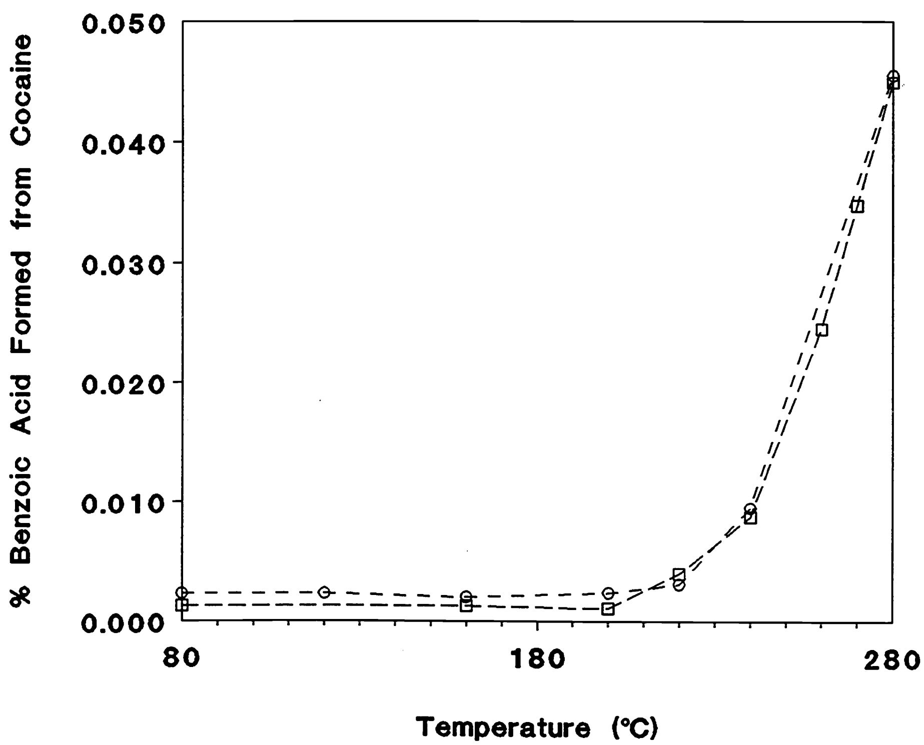


Figure 1. Possible decomposition pathways for cocaine.

Figure 2. Formation of benzoic acid at different temperatures (additional methyl benzoate formation was not detected).



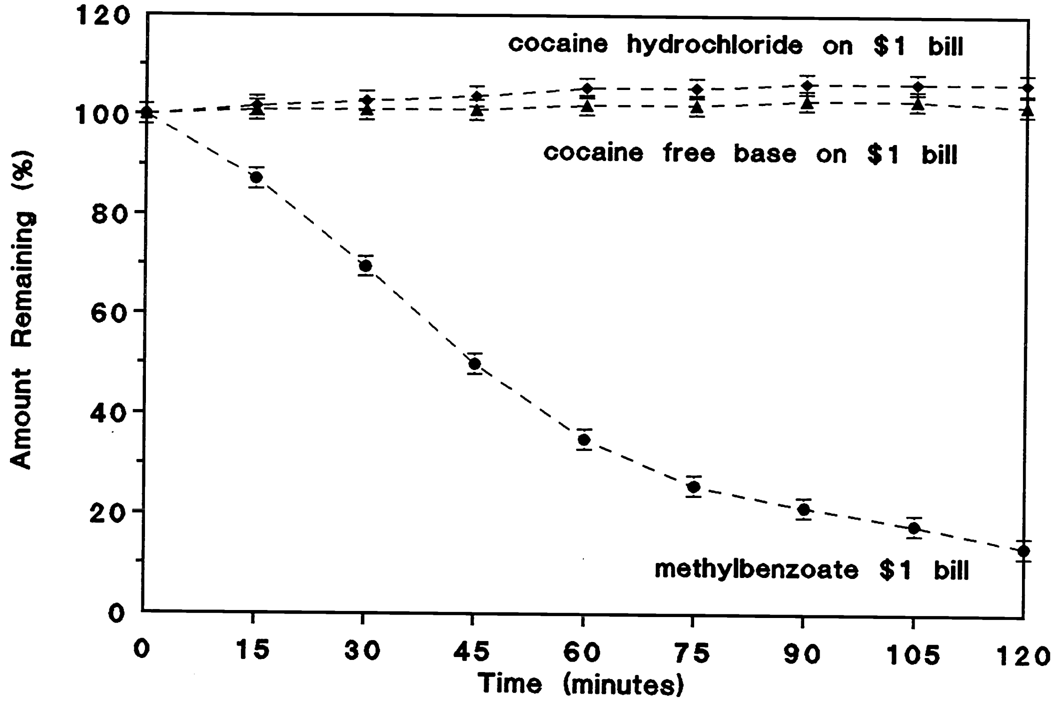


Figure 3. Evaporation of cocaine, cocaine HCl and methyl benzoate from paper currency.

Figure 4. Layout of test room used in this study.

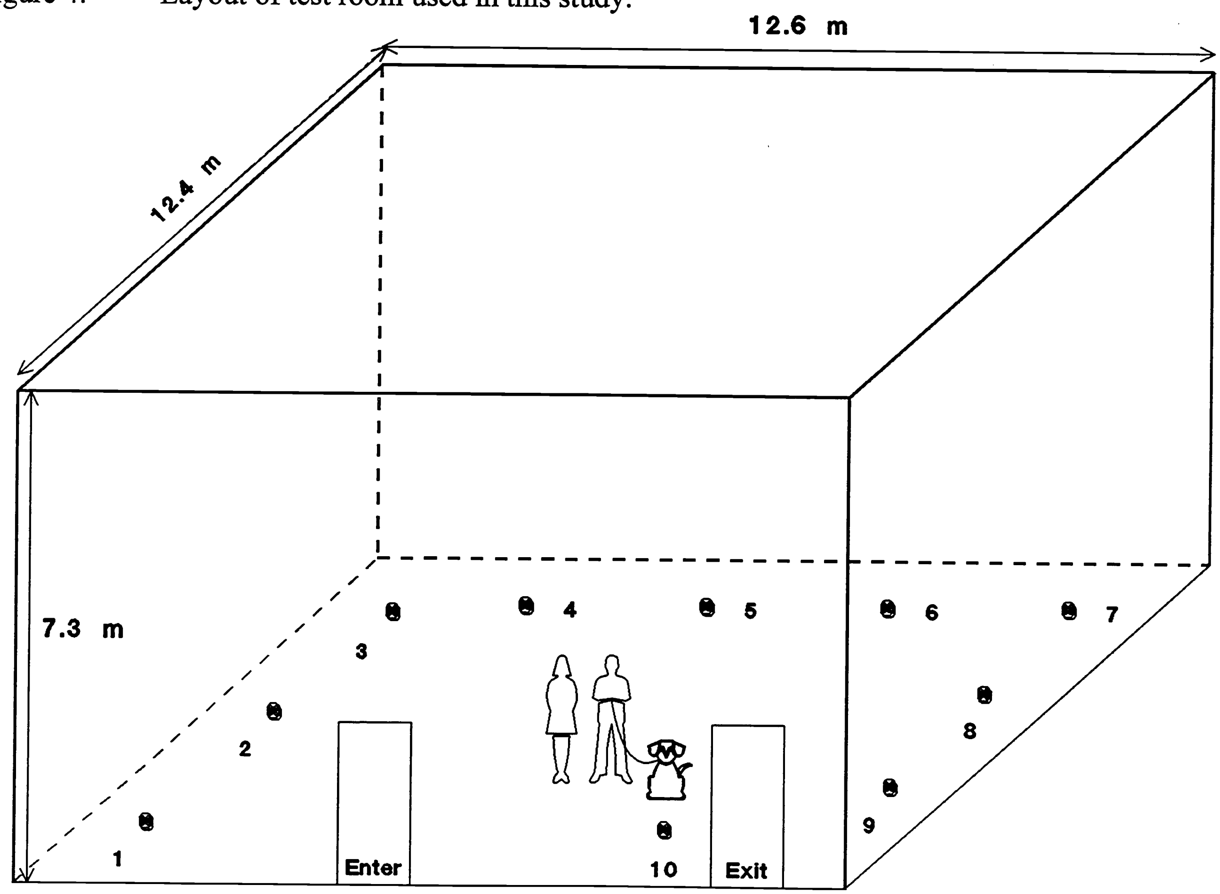


TABLE 2 Summary of K-9 alerts to pharmaceutical grade cocaine HCl and base with added amounts of methyl benzoate

Cocaine added as $CHCl_3$ solution	added by-product‡	Non alert (N)	Alert (A)
0 ng HCl ($CHCl_3$ alone)	0 ng ($CHCl_3$ alone)	1,3,4,6,7,8,10,11,12,14,15	
0.1mg HCl	0 ng	1,3,4,6,7,8,10,11,12,14,15	
1mg HCl	0 ng	1,3,4,6,7,8,10,11,12,14,15	
10 mg HCl	0 ng	1,3,4,6,7,8,10,11,12,14,15	
1g HCl in folded $1 bill	0 ng	1,3,4,7,8,10,11,12,14,15	6
0.1mg HCl	0.1 μg methyl benzoate	1,3,4,6,7,8,10,11,12,14,15	
0.1mg HCl	1 μg methyl benzoate	1,3,4,7,8,11,15	6,10,12,14
0.1mg HCl	10 μg methyl benzoate	4,15	1,3,6,7,8,10,11,12,14
0.1mg HCl	100 μg methyl benzoate	4	1,3,6,7,8,10,11,12,14,15
1g in folded $1 bill	Sigma Pseudo™ Cocaine Scent		1,3,4,6,7,8,10,11,12,14,15
SECOND K-9 RUN			
0 ng Base ($CHCl_3$ alone)	0 ng ($CHCl_3$ alone)	1,3,4,6,7,10,11,12,14,15	
0.1 mg Base	0 ng	1,3,4,6,7,10,11,12,14,15	
1 mg Base	0 ng	1,3,4,6,7,10,11,12,14,15	
10 mg Base	0 ng	1,3,4,6,7,10,11,12,14,15	
1 g Base in folded $1 bill	0 ng	1,3,4,6,7,10,11,14,15	12
0.1 mg Base	0.1 μg methyl benzoate	1,3,4,6,10,11,12,15	7,14
0.1 mg Base	1 μg methyl benzoate	1,3,4,7,11,14,15	6,10,12
0.1 mg Base	10 μg methyl benzoate	7	1,3,4,6,10,11,12,14,15
0.1 mg Base	100 μg methyl benzoate	3	1,4,6,7,10,11,12,14,15
1g in folded $1 bill	Sigma Pseudo™ Cocaine Scent	4	1,3,6,7,10,11,12,14,15

These results have been corroborated with additional field tests using different numbers, types and arrangements of delivery devices. The finding that methyl benzoate, rather than the cocaine itself, is responsible for alerting drug detector dogs is not surprising based on our current knowledge of how detection dogs alert to forensic specimens. When a dog is trained to alert to an item such as a human body, explosives, munitions, accelerants, drugs, currency, etc., the canine is actually being trained to alert to a scent associated with the item rather than the item itself. That scent is composed of volatile compounds or classes of compounds which are detected by the canine in the gaseous state. This is the basis of commercial training aids developed, such as pseudo cocaine, pseudo heroin, etc. which, in fact, contains no controlled substances. The active ingredient in Sigma pseudo™ cocaine is actually methyl benzoate as determined by GC/MS using the ASTM standard method of passive headspace concentration with an activated charcoal strip [7] at 80°C overnight followed by elution with

chloroform. It is well established that canines have a remarkably selective sense of smell, that is, they can be trained to alert to the volatile chemicals associated with the detection material even in the presence of numerous potentially interfering compounds. It is also known that canines can be trained to alert only to specific threshold levels of chemicals. These results indicate that the levels of "pure" cocaine (which always contains finite levels of impurities including methyl benzoate) required to signal an alert for the dogs tested are extremely large.

3. SUMMARY/CONCLUSIONS

Methyl benzoate is rapidly formed in methanolic solutions of cocaine, but did not form to any appreciable extent in solid pharmaceutical grade cocaine. We always found methyl benzoate associated with cocaine. In pharmaceutical grade cocaine from Sigma, methyl benzoate was present at ca. 0.0008% w/w. The threshold level of cocaine and methyl benzoate required for a canine to signal an alert was substantial and reproducible. We have established that the threshold level of detection of cocaine for the canines as tested is greater than 1 g (containing < 0.001% methyl benzoate impurity) with a consistent threshold level of methyl benzoate of around 0.01 g. These levels of cocaine are orders of magnitude higher than the <10 μg/bill average reported for currency in circulation [1], and methyl benzoate, the chemical marker, has not been reported on circulated currency. Methyl benzoate evaporates rapidly from the surface of single dollar bills (>90% evaporates in 120 minutes) while the cocaine remains for very long periods of time. In conclusion, we have found no valid scientific basis for the theory that innocently contaminated currency contains sufficient quantities of cocaine and associated volatile chemicals to signal an alert from a properly trained drug detector dog.

4. ACKNOWLEDGMENTS

The authors would like to thank Dr. Stefan Rose for initiating this project and Sergeant Wesley Dallas of the Metro-Dade Police Department for coordinating the testing of the drug detector dogs.

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Attachment C11

Furton, F.G., Hsu,Y., Luo, T., Norelus, A., and Rose, S., Field and Laboratory Comparison of the Senitivity and Reliability of Cocaine Detction on Currency using Chemical Sensors, Humans, K-9s and SPME/GC/MS/MS Analysis, *Proceedings SPIE*, **2941** (1999).

Field and Laboratory Comparison of the Sensitivity and Reliability of Cocaine Detection on Currency Using Chemical Sensors, Humans, K-9s and SPME/GC/MS/MS Analysis.

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ABSTRACT

Reports that money in general circulation is contaminated with cocaine have resulted in contaminated money theories purporting that any person carrying currency could potentially initiate a drug dog alert. Field tests on dozens of different drug detector dogs with widely varying breeds, ages and training regimes show a consistent threshold level of 1-10 μg of methyl benzoate spiked along with cocaine on U.S. currency or 0.1-1 ng/sec methyl benzoate diffusion required to initiate an alert. No other substance studied to date has initiated consistent responses by the drug dogs studied. The evaporation rate of methyl benzoate from U.S. currency shows an exponential decrease with rates varying considerably (2 to 2000 ng/sec) depending on conditions, decreasing with increasing number of bills and covering of the currency. SPME/GC/MS/MS is capable of detecting femtogram quantities of methyl benzoate, which is much lower than the threshold level of the detector dogs studied to date. Methyl benzoate was identified and quantified in all illicit cocaine specimens analyzed at an average amount of ca. 0.02% (w/w). Human tests revealed a similar threshold level of detection for methyl benzoate but with less reliability than for drug detector dogs. K-9 and human results were compared with results for human test subjects and results using the AromaScanner Model A32S (Aromascan Inc., Hollis, NH). The chemical sensor 'fingerprints' of street cocaine matched those for methyl benzoate and pseudococaine. However, drug odors could not be differentiated electronically with the AromaScanner on U.S. paper currency due, perhaps, to the strong odor pattern for the inks on the currency. Overall, the scientific results indicate that circulated currency, innocently contaminated with μg quantities of cocaine would not cause a properly trained detection canine to signal an alert.

Keywords: Cocaine, Detection, Reliability, Sensitivity, Dogs, Sensors

1. INTRODUCTION

The use of properly trained drug detector dogs to indicate money associated with drug trafficking has recently become a point of contention due to reports that most money in circulation is tainted with trace levels of cocaine[1-3]. These reports have resulted in contaminated money theories purporting that due to this widespread contamination, any person carrying currency could potentially initiate a drug dog alert. The legal significance of this theory ranges from reducing the probative value of drug dog alerts to the complete elimination of drug dog utility if, indeed, canines can alert to any sum of currency. The questions to be answered include: What exactly are the dog alerting to? How selective are the dogs? How sensitive are the dogs? How reliable are the dogs? This theory was relied upon by the 9th U.S. Circuit Court of Appeals which upheld the dismissal of a forfeiture case stating that "... evidence that greater than 75% of all circulated money... is contaminated with drug residue, distinguish this case from our previous cases. We therefore hold that the narcotics detection dog's positive alert to Alexander's money, the packaging [30 rubber band bound stacks of $5, $10, $20, $50 and $100 bills in a plastic bag] and the amount [$30,060] of Alexander's money, and his false accounts of the money's source and his own employment record is insufficient evidence to establish probable cause that the money was connected to drugs as required to warrant forfeiture[4]. Citations in this decision include testimony that 90% of all U.S. cash contains sufficient quantities of cocaine to alert a narcotics detection dog. These conclusions were puzzling in light of the fact that there were neither peer-reviewed studies demonstrating the range of a drug dog's detection capability to drugs nor any statistically significant determinations of the level of cocaine contamination on U.S. currency. The limited studies to date have relied on tiny sample sizes chaotically sampled from specific sites[1-3] which cannot be accurately extrapolated to represent the more than $400 billion in U.S. paper currency in circulation at any given time. Also, since the average lifetime of U.S. paper currency is less than 2 years, studies should be carried out on a regular basis accounting for the constant turnover of paper bills and therefore the variability of any contamination levels as a function of time. A study on cocaine contamination on Canadian currency using a quick ethanol rinsing method found background cocaine levels on 2100 bills of circulated money of ca. 10 nanograms per note and

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SPIE Vol. 3576 • 0277-786X/99/$10.00

currency seized in drug investigations with cocaine levels 50 to over 1000 times the background levels[5]. In a study of surface cocaine contamination of circulated U.S. currency, 2000 bills were tested confirming that cocaine is present on money in general circulation, but not in sufficient quantity to be easily removed except by solvent washing. Paper currency contaminated by counting the money with micrograms of cocaine on the fingertips did yield detectable quantities of cocaine by a shaking method[6]. Current studies on the total solvent extractable amount of cocaine on a small number of bills indicate an average amount of 10 micrograms of cocaine per bill (7.3[1], 22.3[2], and 2.3[3] average micrograms/bill).

We have previously performed field tests on different drug detector dogs and optimized field testing techniques and analytical methods to determine and quantify the drug odor chemicals in illicit narcotics[7]. The purpose of the present work was to confirm the identity of the unique volatile odor chemical(s) emanating from illicit cocaine which canines use for detection. To use SPME/GC/MS^n to detect and quantify cocaine odor chemicals. To compare the reliability and threshold of detection for dogs, humans, and laboratory methods (chemical sensors and GC/MS). And finally, to characterize the evaporation rates of methyl benzoate under different conditions in order to relate the amount of odor detected by K-9's to total illicit drug sample weights including those possible on currency. SPME has many advantages when applied to forensic specimens including allowing for multiple sampling and preservation of the sample while minimizing the risk of sample contamination due to the minimal or no sample handling required by the technique. SPME can yield faster case turnaround time and is often simpler than traditional techniques and readily automated. Also, the lower detection limits possible using SPME allow for confirmation of positive samples which previously went undetected. Finally, the elimination of solvents can save forensic science laboratories money and reduce the risk of analysts being exposed to toxic substances[8].

2. RESULTS AND DISCUSSION

We have now performed field tests on dozens of different drug detector dogs with widely varying breeds, ages and training regimes using different field testing techniques and procedures with similar threshold results obtained. U.S. paper currency was spiked with increasing amounts of cocaine and volatile cocaine by-products. To date, the only chemical found to produce consistent drug dog alerts has been methyl benzoate. Virgin cardboard and galvanized steel boxes containing the spiked currency were placed in a test room with carefully monitored humidity, temperature, airflow, etc. Solutions containing the different amounts of cocaine and by-products were prepared in chloroform solutions and delivered to the currency at least 20 minutes before testing. This time allowed the chloroform to completely dissipate without drastically reducing the amount of odor chemicals present. Solubility study data is summarized in Table 1 illustrating the difficulty in choosing an appropriate solvent for this study. Of the four solvents with the highest solubility for both cocaine HCl and free base, only chloroform proved useable. Both methanol and ethanol reacted with the cocaine (particularly the base form) forming methylbenzoate[7] and ethylbenzoate; whereas, the low volatility of eugenol can alter the evaporation dynamics of the volatile odor chemicals. We have confirmed that the dominant cocaine odor chemical appears to be methyl benzoate via spiked samples as well as controlled delivery devices with threshold levels of 1-10μg spiked methyl benzoate or 0.1-1 ng/sec odor diffusion. None of the dogs tested alerted to by-products other than methyl benzoate and the majority did not alert to synthetic "pure" cocaine unless methyl benzoate is added in the 1 to 10 μg range. Human tests have revealed a similar threshold level of detection for methyl benzoate but with less reliability than for drug detector dogs as seen in Figure 1.

Table 1- The volume of solvent required to dissolve 5 mg of Cocaine at 20.0 °C.

Solvent	**Cocaine, free base**	**Cocaine, HCl form**
Ethanol	< 100 μL	< 100 μL
Methanol	< 100 μL	< 100 μL
Chloroform	< 100 μL	100 - 200 μL
Eugenol	< 100 μL	200 - 300 μL
Acetonitrile	< 100 μL	1400 - 1500 μL
IPA	100 - 200 μL	1100 - 1200 μL
Acetone	< 100 μL	Insoluble
n-Butyl Chloride	< 100 μL	Insoluble
THF	< 100 μL	Insoluble
Toluene	< 100 μL	Insoluble
Ethylene Glycol	Insoluble	100 - 200 μL
Water	Insoluble	< 100 μL

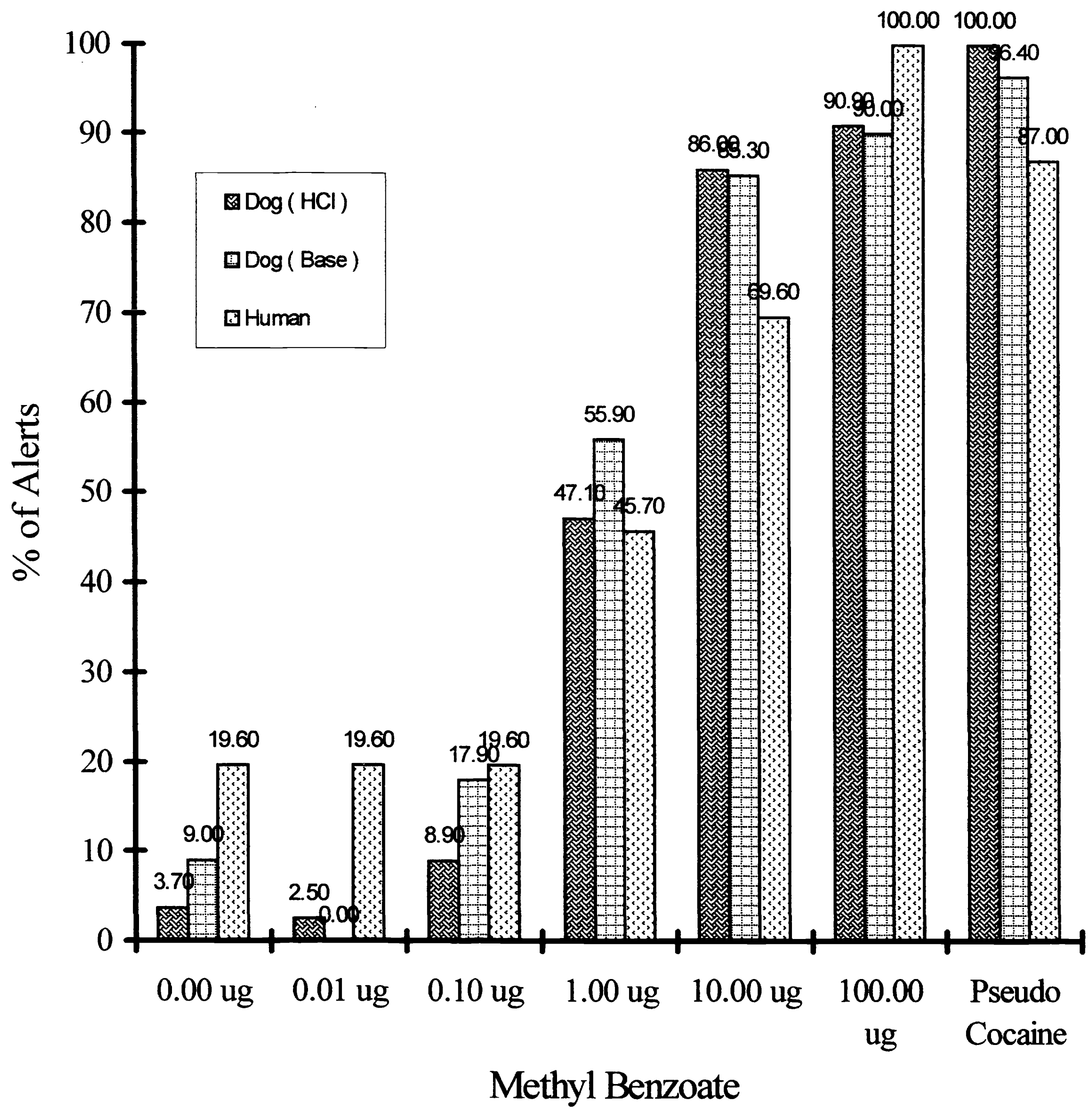

Figure 1 - Summary of cocaine odor alerts by trained detector dogs and humans with increasing amounts of methy benzoate.

K-9 and human results were compared with results using the AromaScanner Model A32S (Aromascan Inc., Hollis, NH). Data from AromaScanner's 32 electrically conducting organic polymer sensor array yielded an Aromamap identifying each sample odor which was compared either as a compilation of the individual sensor outputs or as an average sensor response. The multidimensional 'fingerprint' was compared to other known odors using the measurement of the Euclidian distance, a mathematical compression of multidimensional vectors to a two dimensional representation. More sophisticated data analysis was also performed using self-learning artificial neural network pattern recognition algorithms including feed forward fuzzy networks to identify divergence of a 'fingerprint' from its previously established odor reference library. The 'fingerprints' of street cocaine matched those for methyl benzoate and pseudococaine. However, drug odors could not be differentiated electronically with the AromaScanner on U.S. paper currency due, perhaps, to the strong odor pattern for the inks on the currency as seen in Table 2.

Table 2 - Summary of "Alerts" (at least 90% recognized for pseudo cocaine) by the AromaScanner.

Code	Contained	Pseudo cocaine in Bill	Pseudo Marihuana in Bill	Pseudo Heroin in Bill	Washed Bill	Unrecog-nized
1	0.01μg Methyl Benzoate in White Paper	33%(3/9)	56%(5/9)	11%(1/9)	0%(0/9)	0%(0/9)
2	0.1μg Methyl Benzoate in White Paper	43%(3/7)	43%(3/7)	0%(0/7)	14%(1/7)	0%(0/7)
3	1μg Methyl Benzoate in White Paper	20%(1/5)	60%(3/5)	0%(0/5)	20%(1/5)	0%(0/5)
4	10μg Methyl Benzoate in White Paper	80%(4/5)	20%(1/5)	0%(0/5)	0%(0/5)	0%(0/5)
5	100μg Methyl Benzoate in White Paper	50%(2/4)	50%(2/4)	0%(0/4)	0%(0/4)	0%(0/4)
6	0.01μg Methyl Benzoate in Bill	0%(0/12)	42%(5/12)	25%(3/12)	25%(3/12)	8%(1/12)
7	0.1μg Methyl Benzoate in Bill	38%(3/8)	50%(4/8)	12%(1/8)	0%(0/8)	0%(0/8)
8	1μg Methyl Benzoate in Bill	9%(1/11)	37%(4/11)	27%(3/11)	9%(1/11)	18%(2/11)
9	10μg Methyl Benzoate in Bill	38%(3/8)	38%(3/8)	0%(0/8)	25%(2/8)	0%(0/8)
10	100μg Methyl Benzoate in Bill	17%(1/6)	66%(4/6)	0%(0/6)	17%(1/6)	0%(0/6)
11	1μL Ethyl Benzoate in White Paper	0%(0/4)	50%(2/4)	0%(0/4)	25%(1/4)	25%(1/4)
12	1μL Propyl Benzoate in White Paper	0%(0/3)	100%(3/3)	0%(0/3)	0%(0/3)	0%(0/3)
13	Cocaine HCl Sigma <1g in White Paper	0%(0/1)	0%(0/1)	0%(0/1)	0%(0/1)	100%(1/1)
14	Cocaine Base Sigma <1g in White Paper	0%(0/2)	50%(1/2)	0%(0/2)	0%(0/2)	50%(1/2)
15	Street Drug Sample	75%(3/4)	0%(0/4)	0%(0/4)	25%(1/4)	0%(0/4)

Reference Air: 23°C, Relative Humidity 50%, equilibrated for 10 min; Nose program: 30 Sec reference, 90 sec sampling, 30 sec wash, 60 sec reference; Data was selected from 70 to 90 seconds in each file.

We have also previously demonstrated that the formation of methyl benzoate in relatively pure pharmaceutical grade cocaine specimens is minimal[7] and is likely carried through the coca leaf extraction process and/or is associated with residual solvents present in illicit cocaine samples. The levels of methyl benzote in items including pseudo cocaine scents have been studied by activated charcoal passive headspace concentration with GC/MS analysis and headspace solid phase microextraction with GC/MS/MS analysis. SPME/GC/MS/MS is easily capable of detecting femtogram quantities of methyl benzoate as seen in Figure 2. This amount is much lower than the threshold level of the detector dogs, humans or chemical sensors we have studied to date.

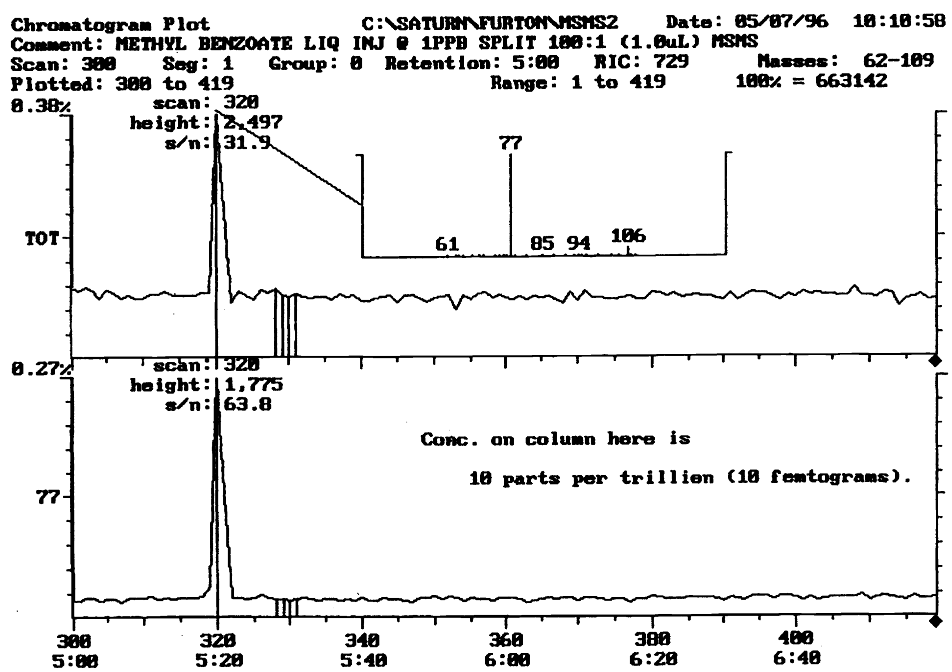

Figure 2 – GC/MS/MS (Varian Saturn 2000) analysis of methyl benzoate showing femtogram detection with high S/N.

Methyl benzoate was identified and quantified in illicit cocaine specimens using SPME/GC with ca. 0.02% (w/w) detected in the limited number of samples studied to date as seen in Table 3.

Table 3 - Concentration of Methyl Benzoate in Street Cocaine Samples

Street Cocaine Sample #	Methyl Benzoate Concentration	
	ppm, SPME Headspace	% (M.B./cocaine), Direct Injection
1	31.1	0.010
2	33.2	0.018
3	58.8	0.036
4	47.6	0.013
Average	43	0.02

We have studied in detail the diffusion of methyl benzoate from U.S. currency under different conditions. Whereas the parent cocaine molecule is non-volatile and can remain on currency for long periods of time, volatile decomposition products such as methyl benzoate dissipate quickly as seen in Figure 3. The evaporation rate of methyl benzoate from U.S. currency has been studied in detail. The amount of methyl benzoate on currency decreased exponentially. Evaporation rates varied considerably (2 to 2000 ng/sec) depending on conditions, decreasing with increasing number of bills and covering of the currency.

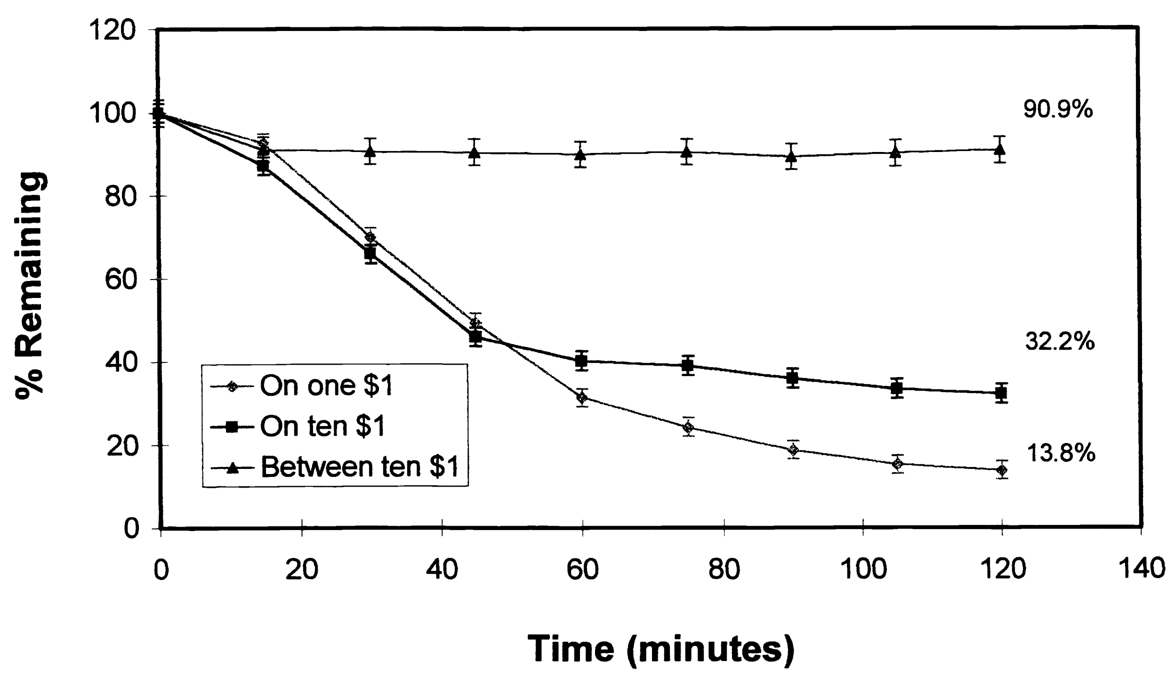

Figure 3 – Evaporation rate of methyl benzoate as a function of time on singles bills, on stacked bills and within stacked bills.

3. CONCLUSIONS

SPME/GC/MS signature profile methods for the detection and quantitation of cocaine odor chemicals has been optimized. Of the fibers tested to date, Carbowax/DVB has been the optimal fiber, providing the highest sensitivity and rapid release of adsorbed analytes into the GC with good linearity over the entire concentration range tested (10-200ppm). Methyl benzoate has been identified and quantified in illicit cocaine specimens but has not been demonstrated to form to any appreciable extent in the solid "pure" form which should be similar to the form found on innocently contaminated paper currency. Methyl benzoate was identified and quantified in illicit cocaine specimens with ca. 0.02% (w/w) detected. The amount of methyl benzoate on currency decreased exponentially. Evaporation rates varied considerably (2 to 2000 ng/sec) depending on conditions, decreasing with increasing number of bills and covering of the currency. We have confirmed the dominant cocaine odor chemical to be methyl benzoate via spiked samples as well as polymeric controlled delivery device with threshold levels of 1-10μg spiked methyl benzoate or 0.1-1 ng/sec odor diffusion.

Calculation from the amount of methyl benzoate required for a reliable detector dog alert (>85% at 10 μg), the amount of methyl benzoate observed in street cocaine sample (ca. 02% w/w) and the diffusion rates of methyl benzoate from individual bills (ca. 10 % remaining after 2 hours) indicate a required amount of recently contaminated cocaine residue of ca. 500 mg cocaine (initially). This amount is ca. 50,000 higher than the amount reported on circulated currency (ca. 10 micrograms/bill). Additionally, the odor produced by contaminated bills stacked together does not increase proportionally to the number of bills, but rather is a function of the available surface area which does not change dramatically and is, in part, limited to the area searchable by the dogs nose. Overall, the scientific results indicate that circulated currency, innocently contaminated with μg quantities of cocaine would not cause a properly trained detection canine to signal an alert even if very large numbers of bills are present.

4. ACKNOWLEDGEMENTS

The authors would like to thank Sergeant Wesley Dallas of the Miami-Dade Police Department for coordinating the testing of the drug detector dog teams and all of the handlers from the various police agencies that participated in this testing. We would also like to thank Varian, Inc. for technical assistance with the GC/MS/MS work.

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Attachment C12

Carter, J.F., Sleeman, R., and Parry, J., The Distribution of Controlled Drugs on Banknotes via Counting Machines, *Forens. Sci. Intnl.*, **132** (2003).

Forensic Science International 132 (2003) 106 112

Forensic Science International

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The distribution of controlled drugs on banknotes via counting machines

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Received 3 May 2002; received in revised form 9 October 2002; accepted 9 October 2002

Abstract

Bundles of paper, similar to sterling banknotes, were counted in banks in England and Wales. Subsequent analysis showed that the counting process, both by machine and by hand, transferred nanogram amounts of cocaine to the paper. Crystalline material, similar to cocaine hydrochloride, could be observed on the surface of the paper following counting. The geographical distribution of contamination broadly followed Government statistics for cocaine usage within the UK. Diacetylmorphine, Δ^9 tetrahydrocannabinol (THC) and 3,4 methylenedioxymethylamphetamine (MDMA) were not detected during this study.

Keywords: Cocaine; Banknotes; Counting machines; Contamination

1. Introduction

A number of studies have shown that a significant proportion of banknotes in worldwide circulation are contaminated with cocaine and, to a lesser extent, other controlled substances [1 7]. Despite these findings and many other reports (e.g. Guardian, 15 November 1994; Sunday Times, 7 January 1996; New Scientist, 13 February 1999), the origin of this contamination has remained a matter for speculation.

Sterling banknotes are printed on a mixture of cotton fibre and linen rag [8]. After a period of use, the characteristics of the banknote fibres change [2,9], giving the appearance of cavities which might enclose small particles, including cocaine. This implies that the retention of controlled substances on banknotes is at least in part due to the physical entrapment of crystalline materials. Other authors have proposed that the retention of controlled substances is due to dissolution in surface inks or grease [10,11], or to chemical binding [5].

In a previous study, particulate material was collected from a large number of banknotes returned to The Bank of England [1] together with dust from a counting machine. Not only were the banknotes found to be contaminated with a range of controlled substances, the dust from the counting machine was also shown to contain significant amounts of cocaine [12]. Other authors have reported the presence of cocaine in counting machines at a bank in Basle, Switzerland [13]. This study demonstrated that counting machines could pass detectable amounts of cocaine from a heavily contaminated banknote to those subsequently counted. The conclusion was, however, that contamination within the counting machine did not account for the widespread occurrence of low levels of cocaine on banknotes.

In order to assess the extent to which counting machines are responsible for the widespread occurrence of controlled substances on banknotes, bundles of paper (with fibre characteristics similar to banknotes) were distributed to banks in England and Wales. The bundles of paper were counted as if they were banknotes and, upon return, analysed for the presence of controlled substances.

2. Materials and methods

A number of commercially available types of papers were examined by electron microscopy in order to find a similar

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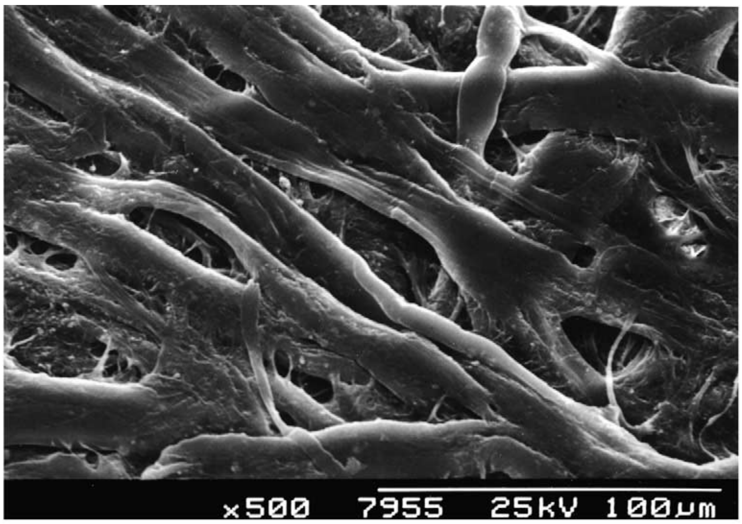
0379 0738/03/$ see front matter
doi:10.1016/S0379 0738(03)00015 X

fibre structure to sterling banknotes. Banknote and paper samples were attached to an aluminium stud using conductive carbon cement. The samples were placed under vacuum for 40 min and sputtered at 20 mA for 4 min to provide a 100 nm gold coating. The samples were observed at 500× magnification with a Hitachi S 2300 Scanning Electron Microscope (SEM) operated at an electron energy of 25 keV.

Conqueror Vellum Laid (100 g/m^2) paper (Arjo Wiggins) was cut into pieces the same size as five pound sterling banknotes (approximately 2.75 in. × 5.25 in.). Using disposable gloves and work surfaces covered with clean aluminium foil, bundles comprising 50 pieces of paper were counted and a small cross marked on one outer surface. These bundles were sealed in bags along with instruction for the bundles to be counted with the marked face on top. Using pseudorandom numbers, 60 branches of Lloyds Bank in England and Wales were selected from a register provided by Lloyds Bank head office. The bundles of paper were sent to these branches together with a request for them to be counted by the usual method employed. Each branch was also supplied with a form to be completed with details of the counting method, machine type (if used) and the number of notes recorded. In early 1998, samples were dispatched via Lloyds internal mail service and returned by Royal Mail. Off cuts of paper were analysed for traces of illicit drugs to ensure that no traces were present on the paper prior to the counting process.

Paper samples were analysed for the presence of cocaine, diacetylmorphine, Δ^9 tetrahydrocannabinol (THC) and 3,4 methylenedioxymethylamphetamine (MDMA) using an Aromic 9100 triple quadrupole mass spectrometer (PE Sciex, Canada) specifically designed for sample introduction by thermal desorption [3]. Paper samples were analysed sequentially by inserting one half of each sheet between two heated metal plates (285 °C) for approximately 1 s. Volatile

(a)



(b)

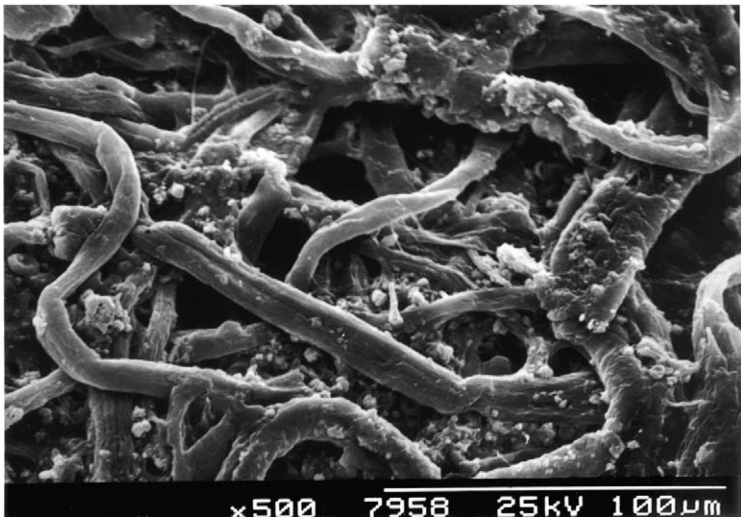


Fig. 1. (a) Sterling banknote surface 500×; (b) Vellum Laid surface 500×; (c) Vellum Laid surface 500× after machine counting.

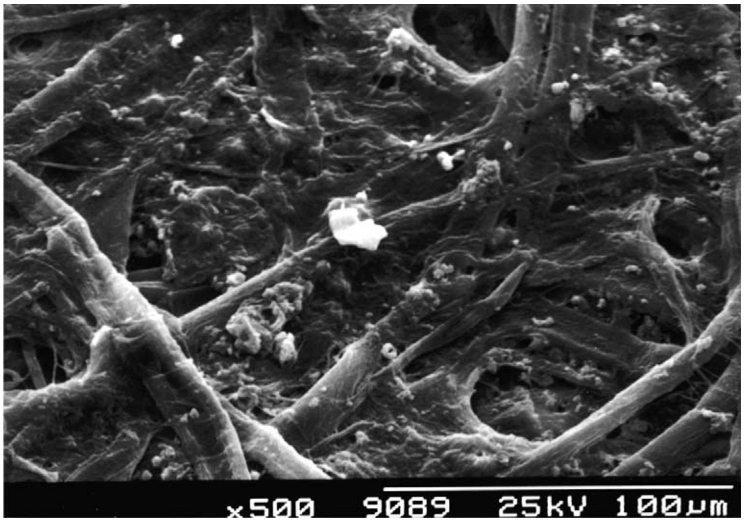
(c)


Fig. 1. (*Continued*).

components liberated by this process were drawn into the atmospheric pressure chemical ionisation (APCI) region of the mass spectrometer. The instrument was operated in selected reaction monitoring (SRM) mode, recording two gas phase ion transitions characteristic of each component [3]. Gas phase ion transitions were recorded sequentially for 20 ms, giving approximately 26 measurements for each compound per sample. The analysis of each paper bundle was preceded by a standard solution containing cocaine (1 ng), diacetylmorphine (10 ng), THC (2.5 ng) and 3,4 methylene dioxymethylamphetamine (1 ng). This was followed by the analysis of a paper off cut.

3. Results

Observation of electron micrographs revealed that Conqueror Vellum Laid paper (Fig. 1b) showed the greatest resemblance to sterling banknotes (Fig. 1a) in terms of fibre structure and the size of cavities available for particles to occupy. It was judged that small surface particles, attributed to pigments, would not influence the retention of controlled substances.

An electron micrograph of the top face of a piece of paper from bundle #24 (opposite end to that analysed) counted in Knightsbridge, London, is shown in Fig. 1c. Particles present on the surface were of a type and size which had not originally been observed. These particles were of a similar size to cocaine hydrochloride crystals (count geometric mean diameter 1.4 μm, with a geometric standard deviation of 2.6 μm) [3]. Although no chemical analysis of individual particles was undertaken at this time, it has been proposed that Raman microscopy could provide a means of analysing single crystals present on the surface of banknotes [14].

Forty three of the 60 paper bundles were returned following counting. Forty of these bundles had been machine counted, three by hand. A number of the banks reported jamming of the paper in automatic counting machines, presumably due to the paper being slightly thicker than banknotes. A number of these banks recounted the paper subsequently by hand (reported as M/H in Table 1).

Of the four controlled substances examined, only cocaine was detected on the paper bundles. The amount of cocaine present on bundles was qualitatively classified in three categories; ''high'' when responses were observed higher than the cocaine standard (i.e. higher than 1 ng per sheet), ''low'' when responses were observed lower than the cocaine standard (i.e. lower than 1 ng per sheet) and ''none'' where no controlled substances were deemed to be present. Table 1 summarises the amount of cocaine detected and the counting method employed at the 43 banks in this study. The authors have estimated that the response for cocaine desorbed from a paper surface is attenuated approximately 20 fold when compared to the injection of a standard solution.

Fig. 2 shows the response of the mass spectrometer to the gas phase transition m/z 304 105 (characteristic of cocaine) for a number of typical bundles analysed during this study. Fig. 2a shows a typical ''high'' assignment obtained from bundle #44 (counted in Fulham, London) and Fig. 2b shows a typical ''none'' assignment obtained from bundle #1 (counted in Peterborough).

A common pattern observed in both ''high'' and ''low'' contaminated bundles was an increase in the response for cocaine from each sheet throughout the bundle (Fig. 2c; counted in London). An unusual pattern of response for cocaine was recorded from bundles #9 and #39 (Fig. 2d; counted in Bristol) in which contamination was observed only on the outer sheets of the bundle.

Table 1
Location of banks returning bundles showing amount of cocaine detected and the counting method

Ref no.	Branch location	Amount	Method
1	Peterborough, PE1	None	M
4	London, NW11	High	M
7	Stockton on Tees, TS18	High	M
8	Edgeware, HA8	High	M/H
9	Camberley, GU15	Low	H
10	London, E1	High	M
11	Eastbourne, BN21	Low	M
12	Hanley, ST1	None	M
13	Christchurch, BH23	Low	M
14	Gosport, PO12	None	M
17	Barnstaple, EX31	None	M
18	North Walsham, NR28	None	M
19	Ivybridge, PL21	Low	M
20	Wells, BS5	Low	M/H
21	Birmingham, B10	None	M
22	Sutton Coldfield, B72	None	M
23	Weston super Mare, BS23	None	M
24	London, SW3	High	M
27	Lydney, GL15	None	M
29	Dorking, RH4	None	M
31	Luton, SY8	Low	M
32	Market Harborough, LE16	Low	M
33	Ealing, W5	Low	M
34	Wadebridge, PL27	None	M
36	Gloucester, GL1	Low	M
37	Altrincham, WA14	None	M
38	Cheltenham, GL50	Low	M
39	Bristol, BS8	Low	H
40	Llanelli, SA15	None	M/H
41	Cranbrook, TN17	Low	M
42	Oswestry, SY11	None	M
44	London, SW6	High	M
45	Ashbourne, DE6	None	M
46	London, SE3	Low	M
47	Warley, B66	None	H
48	West Midlands, CV1	None	M
49	Southampton, SO40	Low	M
51	Oxford, OX3	None	M
54	Wickham, NE16	None	M
55	Shotton, CH5	Low	M
57	Birmingham, B23	Low	M
58	Penzance, TR18	Low	M
60	Southampton, SO18	None	M

M: machine, H: hand.

Fig. 3 shows the geographical distribution of the banks in England and Wales which returned samples for this study.

4. Discussion

Cocaine was the only controlled substance detected, of the four sought, on the bundles of paper returned after counting. Using the classification described, 14% of the counted bundles were deemed to be highly contaminated, 46% of the bundles classified as showing some contamination and 40% no contamination.

Cocaine has an obvious connection with paper currency through the use of rolled banknotes as a means of ingestion. It is axiomatic that large amounts of cocaine present on a single banknote, through direct drug use, could be spread to a very large number of other banknotes in general circulation. This is consistent with empirical findings [13]. A number of controlled substances, other than cocaine, are commonly used in powder form, e.g. diacetylmorphine and amphetamines. These, however, occur as crystals much larger than cocaine [15,16] and may be less readily retained or distributed. In addition, diacetylmorphine and THC are known to be readily hydrolysed [17] which may explain the failure to detect these compounds. It is impossible, therefore, to state whether these compounds were not present in the counting machines or were degraded on the paper surfaces prior to analysis. MDMA is a more stable molecule and should not degrade as rapidly as diacetylmorphine or THC. Both MDMA and THC are, however, used in compressed (tablet or resin) forms which are less likely to yield particulate material which may be retained by banknotes.

A common pattern observed was an increase in the response for cocaine recorded on each sheet throughout a bundle (Fig. 2c), the sheets having passed through the counting machines in the reverse order to which they were analysed. This is attributed to cocaine contamination on components of the counting machine being passed to the paper and diminishing through abrasion during the counting process. The occurrence of crystalline material on bundle #24 (Fig. 1c) was coincident with black marks on the surface of the paper sheets which are assumed to originate from components of the counting machine.

Bundles of paper which had been counted by hand in Bristol (#39, Fig. 2d) and Camberley (#9) showed detectable amounts of cocaine on the outer sheets of the bundles but no discernibly contaminated sheets in the middle of the bundles. Previous studies have concluded that cocaine could not be detected on the hands of bank staff after many hours of handling banknotes [18]. These findings would imply, therefore, that the cocaine detected on hand counted bundles was transferred from working surfaces within the bank.

Although participating banks were selected at random, certain geographical regions were represented more than others. It is assumed that the occurrence of Lloyds banks mirrors population density. The majority of the bundles containing ‘‘high’’ contamination and a significant number of the bundles containing ‘‘low’’ contamination were returned from the London area. Only one bundle returned from a London bank remained uncontaminated. This finding is consistent with UK Government statistics [19] which found that in 2000 London had a significantly higher rate of cocaine usage than other regions of the UK. In general, the use of cocaine and other Class A drugs was highest in affluent urban areas and amongst the richest income

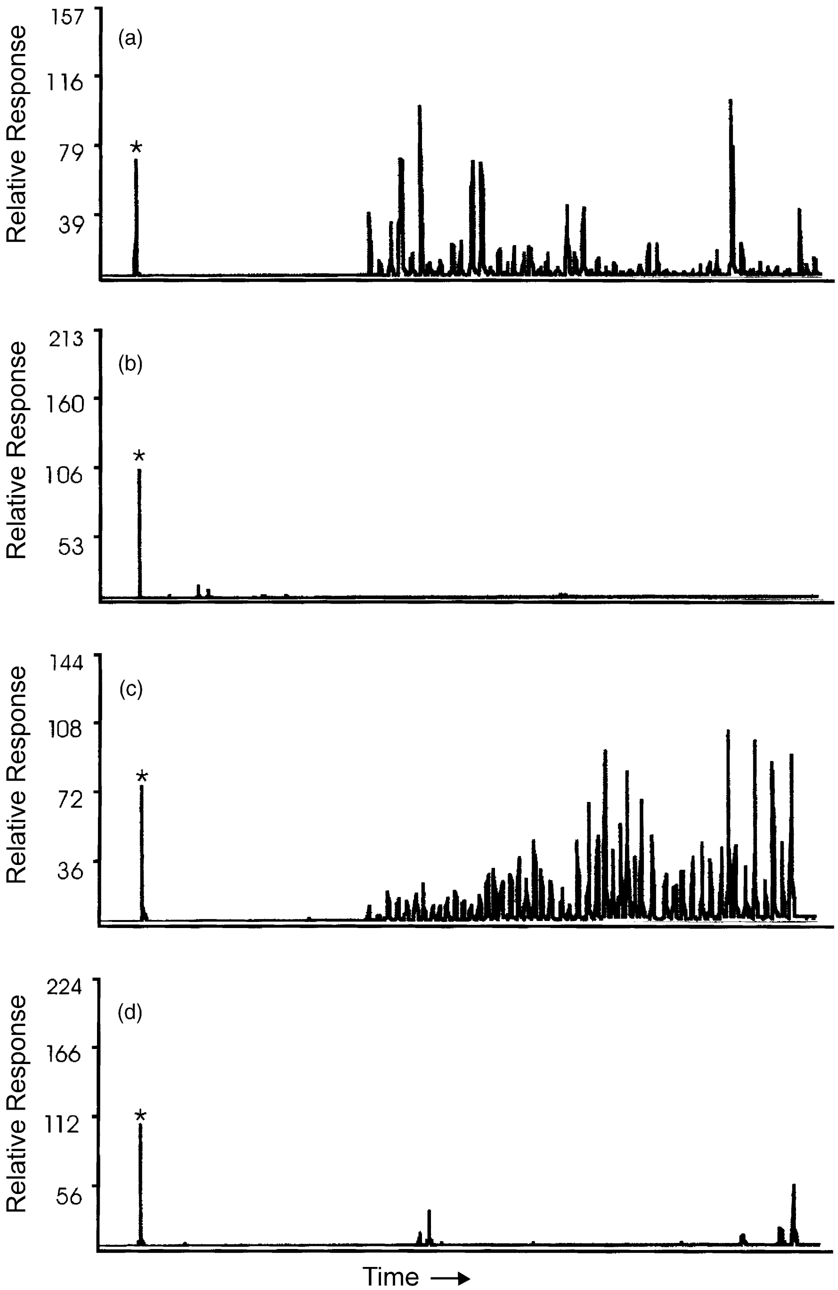


Fig. 2. Mass spectrometer response (*m/z* 304 105) for bundles of paper: (a) #44; (b) #1; (c) #24; and (d) #39. Traces are scaled to 2,000,000 ion counts, (*) indicates response to 1 ng of cocaine standard.

categories. Bundles returned from major population centres in the North and Midland regions of the UK (Liverpool, Birmingham and Manchester) showed little or no contamination, confirming the correlation with cocaine use.

Contaminated bundles returned during this study appear to reflect regional patterns of cocaine usage rather than the frequency of drug seizures (per million population for 1999) [19]. Customs typically seize larger quantities than local police forces and operate at, or soon after, the point of importation [20]. Hence, seizure rates do not reflect the amount of cocaine which may come into contact with banknotes via trading or ingestion. Uncontaminated bundles were returned from both South Wales (#40) and the North East of England (#54) which are areas with a high number of drug seizures [20] but a low level of cocaine usage [19].

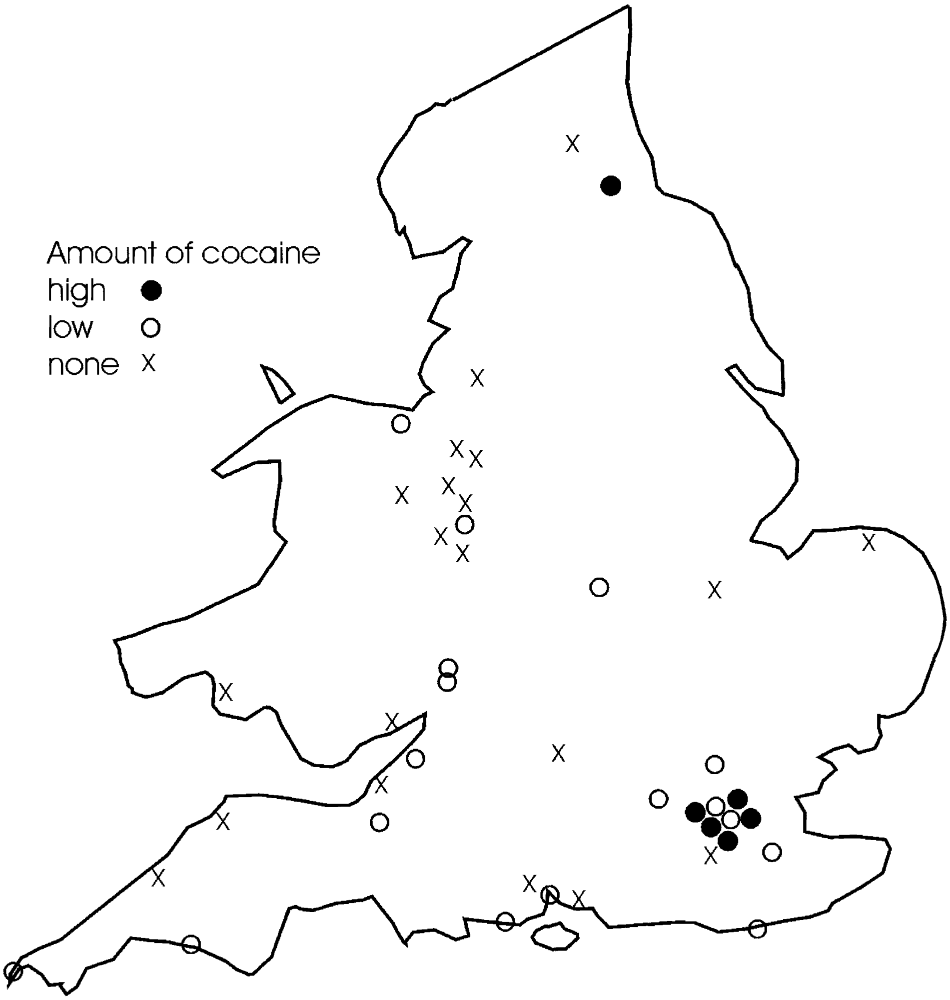


Fig. 3. Locations of participating banks within England and Wales.

The sole contradiction to this pattern was returned from Stockton on Tees (#7) which was the only bundle containing "high" contamination returned from outside the London area. This is an area with moderate drug seizures and limited cocaine usage. The bundle returned from nearby Wickham (#54), which has a higher rate of drug seizures and compar able cocaine usage, showed no detectable contamination.

5. Conclusion

This study has shown that the widespread occurrence of nanogram amounts of cocaine on banknotes is, at least in part, due to transfer by counting machines. To a lesser degree, cocaine may be transferred by hand counting. The extent of cocaine contamination on notes broadly reflected known trends in cocaine usage rather than regional patterns of drug seizures. The presence of large amounts of cocaine or other controlled substances on banknotes is unlikely to be accounted for by this transfer mechanism and may still be viewed as evidence of close contact with a controlled substance.

Acknowledgements

The authors wish to thank Lloyds banks for their assis tance in making this study possible, especially Paula Hodge of the Fishponds, Bristol branch for her help in authorising and co ordinating the distribution of paper samples.

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Attachment C13

Ebejer, K.A., Winn, J., Carter, J.F., Sleeman, R., Parker, J., and Korber, F., The Difference between Drug Money and a “Lifetime’s Savings”, *Forens. Sci. Intnl.*, **167** (2007).

Available online at www.sciencedirect.com
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The difference between drug money and a "lifetime's savings"

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Received 8 June 2006; accepted 14 June 2006
Available online 4 August 2006

Abstract

In many countries, monies suspected of being associated with drug trafficking can be seized by the authorities. One of the ways of investigating this association is through the analysis of seized banknotes for traces of controlled drugs.

We report three studies which may assist the expert in assessing whether banknotes contaminated with diamorphine are part of the general population of notes in circulation or whether they show unusual contamination patterns which require explanation.

Study 1 is based on three plausible contamination scenarios as they may occur during the various stages of an illicit drug transaction and seizure. It shows that notes which have been in direct contact with visible traces of diamorphine show significantly higher contamination to those in more indirect contact with the drug.

Study 2 investigates the transfer of diamorphine from one highly contaminated note to other notes in a bundle over a period of 10 weeks with and without agitation. It was found that the total amount of drug transferred was smaller than 6% and no more than 4 out of a bundle of 10 previously clean notes became lightly contaminated.

Based on extensive background data, study 3 proposes a probabilistic model to assess whether an observed proportion of diamorphine bearing banknotes is likely to have been contaminated by chance. The model predicts that there is only a 0.3% chance that a bundle of 100 notes from the general banknote population contains more than six contaminated specimens.

Jointly, the three studies give useful indications for the spread of contamination throughout a sample and the amounts of heroin which may be expected given plausible contamination scenarios.

Keywords: Diamorphine; Banknotes; Transfer

1. Introduction

The Financial Action Task Force (FATF) lists 40 recommendations, which member countries are committed to implement [1]. The first of these recommendations is to criminalise money laundering on the basis of the United Nations Convention against Illicit Traffic in Narcotic Drugs and Psychotropic Substances, 1988 (the Vienna Convention) [1]. The United Kingdom is one of the 33 members of FATF and, in the UK, the Proceeds of Crime Act allows for the seizure of cash reasonably suspected to be gained unlawfully [2]. Where illegal drug activity is suspected, the results of the analysis of the banknotes for traces of illicit substances can be used as circumstantial evidence. However, this requires that the banknotes be distinguishable from those typically in general circulation [3].

Banknote analysis by gas chromatography mass spectrometry (GC/MS) has been performed successfully by a number of workers [3 7]. A major drawback of any method based on GC/MS is the long preparation and analysis time required, in comparison with thermal desorption atmospheric pressure chemical ionisation tandem mass spectrometry (APCI MS/MS) [8 10]. The latter is currently the method of choice for law enforcement agencies in the UK. The speed of this technique has allowed a huge number of banknotes from general circulation, so called "background" banknotes, to be analysed individually. This background database of illicit drug traces detected on banknotes from the UK is maintained and routinely used for comparison with drug traces detected on banknotes seized from suspects thought to be involved in illegal drug activities.

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0379 0738/$ see front matter
doi:10.1016/j.forsciint.2006.06.039

Since the background database contains data from individual banknotes, the contamination of bundles of banknotes can be described in terms of both the quantity of drug contamination [11] and the proportion of banknotes in a bundle with detectable traces of a drug [12]. The advantage of having two complementary methods for data interpretation is that either or both can be employed as appropriate to the drug of interest. Cocaine, for instance, occurs on virtually all Bank of England banknotes in general circulation [10]. Therefore, any attempt to differentiate on the basis of contaminated proportion is futile. Such an approach, however, is valid for diamorphine contamination, where the drug occurs on much smaller numbers of banknotes in the background.

The proportion of banknotes with diamorphine contamination has been used as the discriminating factor in a large number of legal proceedings, but this forms only one aspect of the evidence. Defendants commonly claim that large quantities of banknotes in their possession represent a lifetime's savings, a gift, an inheritance, the profits from trading in a grey economy, etc. They also maintain that the diamorphine contamination came to be on the banknotes by mechanisms unknown and unrelated to them. It is, therefore, useful to consider not only whether a seizure is contaminated to an unusual degree, but also to assess the pattern of contamination on the seized banknotes and the likelihood that they became contaminated through means other than illegal drug activity.

In this paper, we report on the contamination patterns of banknotes subjected to three plausible scenarios associated with activities related to drug dealing. A further study investigated the transfer of diamorphine from a highly contaminated note to adjacent notes over a period of 10 weeks. Lastly, a probabilistic model was fitted to the diamorphine contamination background database to permit a more reliable assessment of which contamination proportions may be classed as ''unusual''.

2. Materials, methods, techniques

All banknote analyses were performed using triple quadrupole mass spectrometers (MDS Sciex, Concorde, ON., Canada) with custom-built thermal desorption inlets consisting of two metal plates heated to 285 °C. Insertion of a banknote or paper swab, for approximately 1 s, between the metal plates caused volatilisation of debris including diamorphine, from the sample. The vapours became entrained in ambient air flowing into the APCI source of the instrument [12]. The mass spectrometer was programmed to monitor two product ions from the protonated molecule of diamorphine (*m/z* 370). The product ions of interest for diamorphine were *m/z* 328 and *m/z* 268. Peak areas were obtained from the extracted ion chromatograms (Analyst 1.4, MDS Sciex, Concorde, ON., Canada) using software written in MATLAB (release 12, The Mathworks, Natick, MA, USA) for the identification and integration of peaks [11].

Instrument performance was monitored by injection of a solution containing 2 ng of diamorphine in methanol. Swabs from the analyst's gloves and worktop were analysed, and shown to be free from diamorphine, prior to making contact with the banknotes.

The advantage of the described analytical technique is that a single banknote can be analysed twice once for each end. The results from two ends of an individual banknote may vary, due to localised deposits. However, average results from the two ends are found to converge when large numbers of banknotes are analysed (unpublished results). In forensic casework, exhibits that have been analysed once can be reanalysed if required.

2.1. Study 1 primary, secondary and tertiary transfer to banknotes

British banknotes, being composed of a mixture of cotton and linen, were shown to be simulated best by cotton paper, rather than wood pulp based products as previously used [13]. A study of diamorphine transfer showed cotton paper to have similar properties to banknotes (average correlation coefficient 0.84) in contrast to a wood pulp based copy paper (average correlation coefficient 0.79) (unpublished results).

Contaminated banknotes were modelled using Crane's Crest cotton paper (100% rag, 90GSM, Crane & Co. Inc. Dalton, MA). The paper was cut to the approximate size of a £10 sterling banknote. This substitution removed the need to correct for the natural background levels of drugs on banknotes and also eliminated differences between the quality of banknotes (e.g. worn, new, dirty, clean). Indeed, it proved difficult to obtain a sufficiently large number of banknotes in a similar physical condition.

Three stages were used to simulate different steps in a drug-dealing scenario. Each stage was physically isolated on a 30 cm × 30 cm sheet of laminated chipboard of a type commonly used in furniture manufacture. The intention was that the amounts of diamorphine present on each of the three surfaces were representative of those transferred by primary, secondary and tertiary contacts with the drug.

In the first stage, approximately 10 mg portions of street heroin (Avon & Somerset Constabulary, Scientific Investigations, approximately 10% diamorphine) were weighed into cigarette papers to make 10 typical street-sized dealer's ''wraps''. Samples were weighed using Diamond brand ''professional mini'' electronic scales, typical of the variety seized from suspected drugs dealers. Ten cotton paper notes were counted onto this surface into a single pile, which was then inverted and the notes recounted. Subsequently, the notes were analysed.

In the second stage the wraps, prepared above, were placed on a surface previously shown to be clean. Ten cotton paper notes were then counted, as before, onto this surface and then again onto a third, clean surface prior to analysis.

In the third stage, 10 cotton paper notes were counted onto the third surface and analysed.

Gloves were worn during the weighing and wrapping of heroin, but cotton paper notes were counted using bare hands because this appeared more realistic. Hands were washed with copious amounts of warm water between counting stages. The

entire sequence was repeated using clean surfaces and cling film to manufacture the wraps.

2.2. Study 2 transfer between banknotes

To simulate the contaminants as realistically as possible, particulate street heroin and household dust were used to contaminate clean paper. Household dust is likely to contain skin oils as found on banknotes [10] and may be expected to simulate the daily environment to which banknotes are exposed. A quantity of street heroin (as above) was mixed in a plastic receptacle with a dust taken from a domestic vacuum cleaner and passed though a 1.7 mm sieve followed by a 0.5 mm sieve.

A number of cotton paper notes were agitated manually for a period of several minutes with the spiked dust. The notes were withdrawn, shaken to remove loose deposits and tested and the response to diamorphine was measured. The amount of heroin in the dust was adjusted until the response was approximately at the mid-point of the dynamic range of the MS MS instrument. This mixture was then used to spike further cotton paper notes in the same manner. A few of the spiked notes were analysed to check that sufficient diamorphine had been transferred to mimic the contamination levels typically detected on contaminated banknotes observed in case work.

A sample consisting of 120 banknotes (£10 denomination) was drawn over the counter from a bank in Bristol, UK and one end of each note analysed for the presence of diamorphine. A record was kept of the order in which the notes were analysed, and this order was maintained while dividing the banknotes into 12 groups of 10 banknotes each. A spiked cotton note was then inserted exactly in the middle of each bundle (Fig. 3), and the bundles were sealed inside close fitting zip-lock bags. All bags were then sealed inside a tamper-evident bag and stored in the dark.

Over the course of 10 weeks, each bundle, except two control bundles, was counted on a weekly basis. The zip-lock bags were distributed to different co-workers who opened the bag and counted out the banknotes, including the spiked note, at least once, in any manner they pleased, but without altering the sequence of notes within the bundle. After a few minutes, the banknotes were returned to their respective zip-lock bags. In weeks 2, 4, 6, 8 and 10, two bundles were analysed and removed from the pool. The analysis was performed on both ends of each note. The remaining samples were resealed inside a tamper-evident bag and returned to dark storage.

2.3. Study 3 comparing contamination with the background database

One hundred and eighty-six bundles of banknotes, each comprising 100 banknotes or more, were selected from the background database. Diamorphine contamination on both ends of the banknotes was measured using the procedure described. The mean number of banknotes in each sample that gave a true positive response for diamorphine was determined [12]. This number was then normalised to the total number of banknotes in the sample (true positives per 100 banknotes) to correct for sample size variation, and rounded to the nearest integer.

The arithmetic mean of the number of contaminated banknotes per 100 (μ) was also determined from the same data set. A Poisson distribution, using μ as the predicted outcome (λ) was then generated and compared to the background database. Data were processed using SYSTAT 11 for Windows (SYSTAT software Inc., Richmond, CA).

3. Results

3.1. Study 1 primary, secondary and tertiary transfer to banknotes

Fig. 1(a and b) show the intensity of the diamorphine product ions, as a function of time, detected on ten cotton paper notes from each of the three stages simulated. The trends observed for cigarette paper wraps and cling film wraps can better be visualised from a histogram representing the relative, average diamorphine transfer for each category (Fig. 2). The number of contaminated notes decreases with the level of contact in both the cigarette paper and cling film wrap scenarios. Secondary

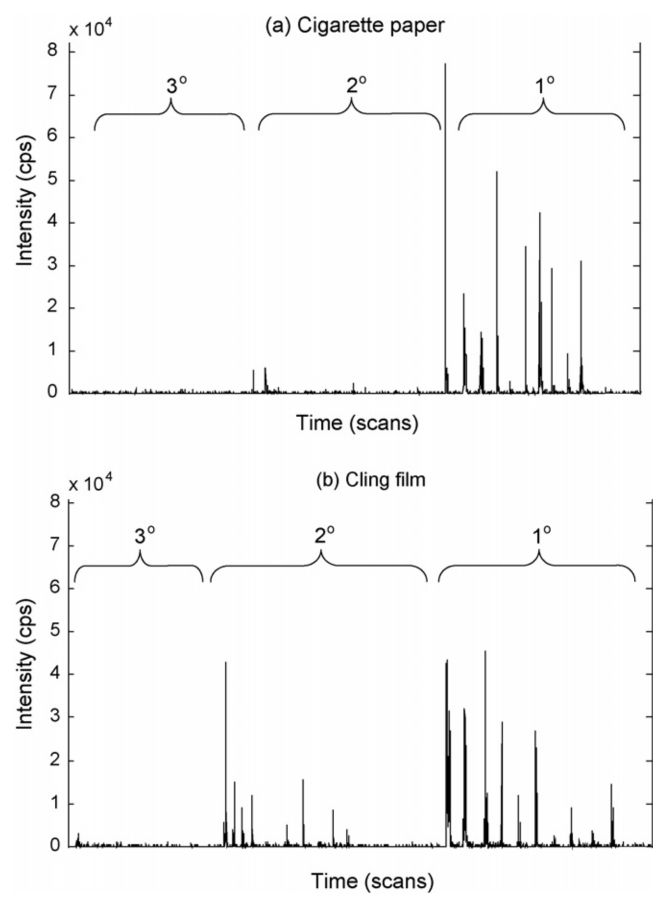

Fig. 1. Ion counts recorded for the m/z 268 product ion of diamorphine on cotton paper notes counted on (tertiary, secondary and primary) surfaces used to simulate a drug deal using wraps of (a) cigarette paper (b) cling film. The same trend was observed for the second ion monitored (m/z 328).

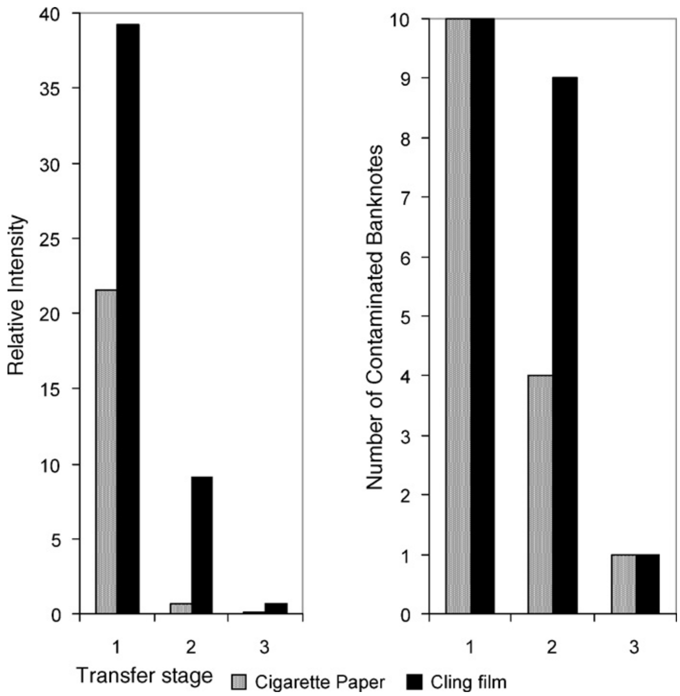

Fig. 2. The mean responses for the product ions of diamorphine (summed) detected on banknotes counted onto primary, secondary and tertiary stage surfaces.

transfer from cigarette paper wraps produced about half the number of contaminated notes compared to primary transfer. However, for secondary transfer from cling film wraps almost all the notes in the bundle were contaminated, making it difficult to distinguish primary from secondary transfer on the basis of contamination proportion. Tertiary transfer resulted in a single note becoming contaminated from both types of wrapping material.

The relative intensity plot (Fig. 2) shows that the quantities transferred in the various stages differ considerably and an analysis of variance was performed to establish whether the apparent differences are statistically significant. For a given experimental situation, i.e. for each bundle, the distribution of contamination (peak areas) was found to be approximately log-normal. Therefore a two factor analysis with replication (Microsoft Excel 97) and a Tukey test [14] were performed on the logarithms of the peak areas for the m/z 268 and the m/z 328 product ions. The tests established which parameters influence the mean quantity of drug detected on each analysed bundle and whether one can distinguish the various stages of a drugs deal by the quantity of drug transferred.

In the two factor analysis the main factor was the type of transfer scenario (primary, secondary or tertiary transfer). This variable was responsible for approximately 65% of the total variation in the sample set, as measured by the total sum of squares. Its contribution was more than twice as large as that from random fluctuations, showing that this factor is highly significant ($p < 10^{-14}$). The second factor analysed was the type of material used for the wraps. This factor was responsible for less than 5% to the variation but was still a statistically significant source of difference ($p < 0.01$). As might be expected, the interaction between the two factors is small and at any reasonably chosen level of significance the two factors are not correlated.

The Tukey test identified which of the bundles were significantly different with regards to the amount of drug transferred. The test was performed independently for each ion on all six bundles (three transfer types and two wrap materials) at a confidence level of 95%. The test reliably differentiated between primary transfer scenarios in one group and secondary and tertiary transfer scenarios in a second group, i.e. the notes in direct contact with spilled heroin on the cutting table were significantly more contaminated than those from indirectly contaminated bundles. Despite the apparent trend towards less contamination for the tertiary stage it was not possible to differentiate between secondary and tertiary transfer, based solely on the quantity of material transferred, at the 95% confidence level. By reference to Fig. 2 it is, however, immediately clear that secondary and tertiary transfer can be distinguished on the basis of the proportion of contaminated notes.

3.2. Study 2 transfer between banknotes

A signal to noise ratio of 4.5 was used as a threshold for peak detection. Peak areas for the two ions were summed. The real peak data for each end of a given banknote or spiked note were also summed to give a better representation of the total diamorphine contamination detected on the note. Every two weeks average of the data from two bundles, was calculated to arrive at a single value for the response of the MS/MS instrument to a banknote in a given environment.

The diamorphine contamination detected on banknotes at a given sequential distance (Fig. 3) from the spiked note was

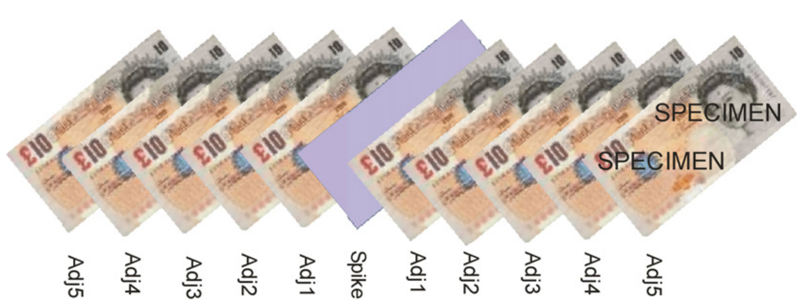

Fig. 3. Arrangement of banknotes and cotton paper spike in study 2.

calculated as the total contamination on the two contributing notes. The degree to which diamorphine was transferred or retained was expressed as a proportion of the total amount of diamorphine detected (Fig. 4).

In addition, the number of contaminated banknotes in a bundle was plotted as a function of time (bar chart, Fig. 5). The amount of diamorphine detected on the spiked paper, corrected for instrument variation, was also plotted (line graph, Fig. 5).

3.3. Study 3 comparing contamination with the background database

A total of 186 bundles of banknotes in the background database were found to have an average of 1.85 true positives for diamorphine per 100 banknotes. The number of contaminated banknotes in a bundle was shown to follow a Poisson distribution ($\chi^2 = 2.30$, $p = 0.81$) (Fig. 6). Using this Poisson distribution it is possible to estimate the chance that a sample of banknotes with a high degree of diamorphine contamination has been drawn from the background by chance. The highest proportions of contaminated banknotes observed in the 186 backgrounds were two incidents of 6 contaminated banknotes per 100, and a single incident of 8 notes per 100. These upper values are consistent with those predicted by a Poisson distribution based on a predicted outcome (λ) of 1.85 contaminated notes per 100 (Table 1).

The chance of a seizure having 10 contaminated banknotes per 100, or higher, is very slight if the banknotes had a similar history to that experienced by banknotes in the background

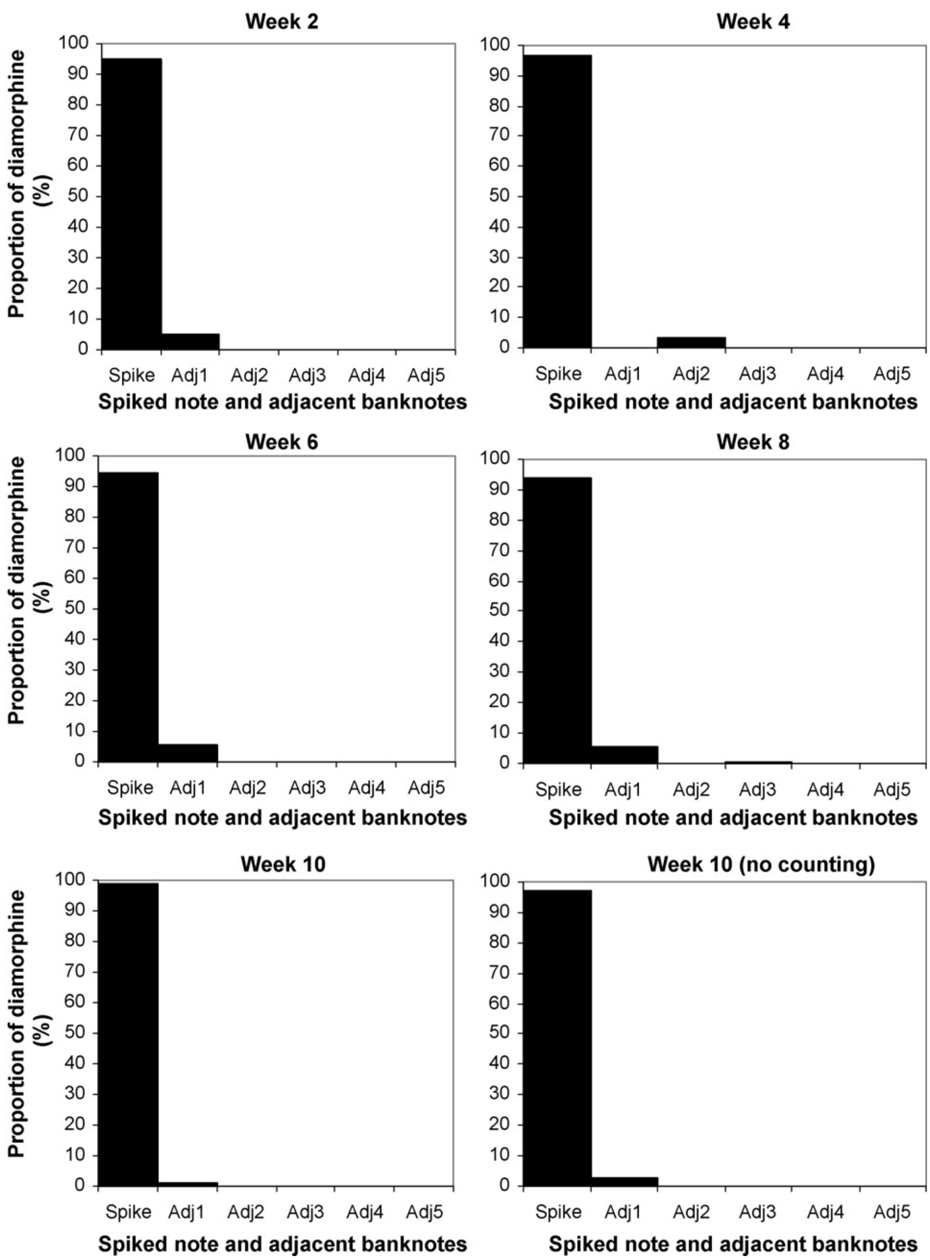

Fig. 4. Proportion of diamorphine detected on the spike and adjacent banknotes.

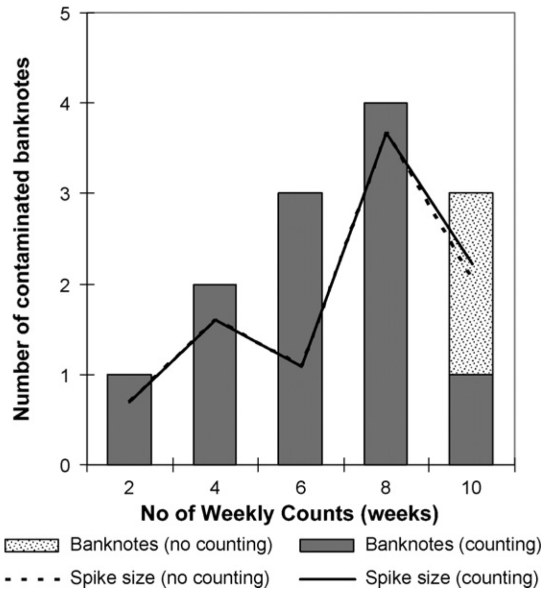

Fig. 5. Total number of contaminated banknotes (excluding the spiked notes) detected from two bundles of ten banknotes after introducing a spiked note to each bundle and counting on a weekly basis.

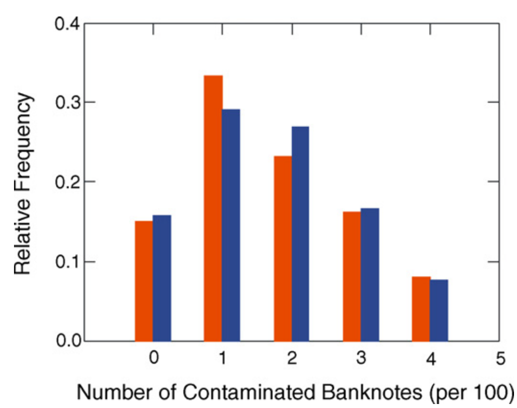

Fig. 6. Data observed (red) and predicted by a Poisson distribution (blue) for diamorphine contamination of banknotes taken from general circulation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

database. This implies that an alternative explanation is called for.

4. Discussion

Although quantitative amounts of diamorphine could easily have been applied to the simulated notes as solutions, it was considered that the use of impure, solid 'street heroin' samples would provide a more realistic model for 'real-life' heroin contamination in several ways. First, solutions are likely to 'wick' into the fibres of the paper, rather than remaining on the paper surface, or being trapped in the interstices between fibres as would be expected of particles. In turn, this may render the diamorphine less amenable to liberation by thermal desorption. Secondly, the evaporation of the solvent would lead to the formation of smaller crystal sizes than would typically be present in 'street heroin', and most certainly would not

Table 1
The chance that a given number of contaminated banknotes are drawn from general circulation (given a Poisson distribution with λ 1.85)

Number of contaminated banknotes in a sample of 100	Approximate odds of drawing these by chance
0	6:1
1	3:1
2	4:1
3	6:1
4	12:1
5	33:1
6	100:1
8	2000:1
10	50,000:1

represent a true reflection of the range of particle sizes found in the real world [15]. It is reasonable to speculate that larger crystals may transfer more easily between banknotes as they become trapped less readily between the fibres. Since most of the mass transferred will be in the form of larger crystals, applying diamorphine in solution is likely to represent a poor model for real world contamination, even though the spiking would be more quantitative and less variable. Further, application of a solution could be achieved by dipping (leading to homogeneous distribution of the material) or via a syringe (resulting in contamination concentrated in certain areas), neither of which accurately reflects the likely distribution of particulate material. Hence, although the method used to spike cotton notes lacks both repeatability and reproducibility it was considered the best model available.

In study 1 it was, perhaps, unsurprising that cotton notes counted on a surface with visible deposits of heroin retained significant traces of diamorphine which could subsequently be liberated by thermal desorption. The intensity of the responses observed from these notes was similar to those observed when analysing banknotes from suspected drugs dealers. Wraps prepared on the same surface would be exposed to similar amounts of heroin and can reasonably be expected to retain external deposits. Some proportion of these deposits may then fall onto the stage 2 surface, becoming available for retention by the cotton notes counted on this surface.

From Figs. 1 and 2, it is apparent that some secondary transfer to the cotton notes has indeed occurred. Cotton notes counted after cigarette paper wraps had been in contact with the surface, however, retained much smaller traces of diamorphine than those counted after cling film wraps had been in contact with the surface.

Different mechanisms are undoubtedly responsible for the retention of particles by paper and by cling film. In the latter case the mechanism is almost certainly electrostatic, possibly leading to larger initial retention and a larger resulting deposit. In addition, the retention mechanism of the cling film may be weaker than the paper, resulting in a deposit that is more readily lost. In contrast, particles retained by paper surfaces are likely to be retained as inclusions in surface features [10] or by dissolution in surface dirt (finger grease, etc.) or water associated with the cellulose. These different mechanisms may well exhibit different affinities for different crystal sizes

resulting in preferential retention of different materials. It is possible that deposits retained by both the cotton and cigarette papers are strongly bound, not readily lost to the stage 2 and 3 surfaces and, therefore, not available for subsequent retention by clean cotton notes. This conjecture is supported by the small deposits retained by cotton notes counted on the third surface.

The statistical analysis shows that the quantities of drugs transferred to the notes directly from the cutting table are significantly different from those transferred at the secondary and tertiary stages. This information would be of limited value unless the study was performed at similar primary surface contamination levels as observed in real life scenarios. Whilst this cannot be asserted, the aforementioned similarity in intensity observed in seized samples gives an indication that this may indeed be the case.

In study 2 the source of contamination (the spike) was easily identifiable at every stage of counting. The amount of diamorphine remaining on the spiked note through the study varied from 94 to 99% of the total amount detected on all banknotes in a bundle. Transfer occurred primarily from the spiked note to one or both banknotes immediately adjacent (Adj1) to it in a bundle. Where the spiked note lost as much as 6% of its diamorphine to other banknotes in the bundle, the amount detected on a single adjacent banknote was less than 6%. This is in line with previous findings [10]. After 4 weeks and after 8 weeks, diamorphine was also detected on a banknote two steps (Adj2) and three steps (Adj3) away from the spiked note, respectively. On banknotes between these and the spiked note, no contamination was detected, suggesting that transfer in these instances may have occurred via the inner surface of the zip-lock bag in which a bundle was stored, or via the counting surface.

Since a single source of contamination was, in general, found to contaminate up to two banknotes with diamorphine, it might be argued that two-thirds of the contamination detected in an exhibit could have arisen by this process. This would assume minimal bunching of contaminated notes in a bundle. To have an appreciable effect, banknotes with "primary" contamination would need to be dispersed throughout a bundle of otherwise uncontaminated banknotes.

In the first 8 weeks of the study, the number of contaminated banknotes in every bundle of 20 notes increased with the number of counting events. This was, however, concomitant with a general increase in the diamorphine contamination of the spiked paper in these bundles. One of the drawbacks of using a solid material to create the spiked notes was that there was no way to precisely regulate the amount of drug present on them. The observed trend in the spike note intensity reflects the random variations in this process.

A combination of the amount of drug initially present on the spiked note, and the number of mixing events, is probably closer to the truth. In the 10th week, a sudden drop in the number of contaminated banknotes in the bundles that had been subjected to weekly counting corresponded with a fall in the amount of contamination on the spiked paper. However, the spike sizes were similar in the counted and uncounted control samples, but the number of contaminated banknotes in that sample was higher. One explanation may be that the majority of transfer occurs in the first contact event, experienced by all bundles when the spiked paper was introduced. Subsequently, transfer is minimal, and each counting occasion results in losses from the bundles and more exposure to light and moist air that could increase the natural degradation of the diamorphine [16 18].

In study 3, the database against which comparisons were made comprises mainly samples drawn from over the counter at banks throughout the UK. A smaller component of the database consists of samples from small businesses such as pubs and shops. These are all considered to be representative of banknotes in general circulation. There has been extensive discussion on the degree to which banknotes mix in general circulation [12]. If the small proportion of banknotes contaminated with diamorphine in general circulation is indeed randomly distributed, then the probability of drawing a sample bearing a given number of contaminated banknotes can be described by a Poisson distribution [19]. This is a good approximation for a binomial probability for large numbers where the event of interest occurs with a low probability. There is no need to specify sample size as long as an expected frequency can be calculated for the number of events observed [19].

The study has illustrated that the chance of detecting highly contaminated bundles of banknotes in samples drawn at random from general circulation, is slight. Indeed, the detection of high frequencies of diamorphine contamination implies that the banknotes may have originated from an isolated population, such as drug dealers or drug users. It is possible that contaminated monies could, for example, be paid into a bank and subsequently withdrawn by an innocent individual prior to mixing. Extensive mixing of such banknotes with banknotes in general circulation would account for the low frequency observed in the database. Finding a highly contaminated bundle therefore cries out for an explanation.

5. Conclusions

The limited studies discussed in this paper have produced some interesting findings, although further work will be necessary to strengthen the conclusions that can be drawn. Cotton notes in direct contact with surfaces bearing visible deposits of heroin were found to retain significant amounts diamorphine. Such deposits did not transfer readily between banknotes when mixed and counted in bundles (less than 6% transfer). A single highly contaminated note is unlikely to contaminate more than the two adjacent banknotes. Since only a small proportion of the initial deposit is transferred the primary and secondary deposits are readily distinguishable. The extent of transfer between banknotes appears to be dependent upon the amount of material on the initial spiked note but may also be dependent upon the physical handling of the notes, which can increase or decrease the size of secondary deposits.

Other materials, e.g. cling film and cigarette papers can transfer deposits to a secondary surface where they are available for retention by cotton notes. These secondary deposits do not then transfer readily to other surfaces to become available for retention by other notes. Hence, counting contaminated notes on a surface along with clean notes does not appear to spread

contamination. These data suggest that two retention mechanisms are involved, one by which material is strongly retained and one by which material is weakly retained and readily lost; the latter providing a means of secondary transfer.

As a result of poor transfer, only a very limited number of banknotes in general circulation (approximately 2%) carry traces of diamorphine. The mixing and circulation of banknotes provides a mechanism by which these contaminated notes are randomly dispersed in the general population producing a homogeneous background. Knowing the average number of contaminated banknotes in the background it is, therefore, possible to estimate the chance of drawing a given number of contaminated banknotes using a Poisson distribution. Using this predictor, the chance of drawing a large proportion is very slight. Even if the contamination on these banknotes had spread to adjacent notes, the overall conclusion of this study is that banknotes known to have been in direct contact with deposits of heroin can be distinguished from those contaminated by secondary or tertiary processes.

Acknowledgements

The authors wish to thank the following people for their help. Lauren Baba of the Centre for Chemometrics, School of Chemistry, University of Bristol for her work in comparing the distribution of contamination on banknotes. Paula Hodge and Martin Scrase of Lloyds TSB for information about the circulation of UK banknotes. MSA staff for populating the background database.

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Attachment C14

Wimmer, K., and Schneider, S., Screening for Illicit Drugs on Euro Banknotes by LC-MS/MS, *Forens. Sci. Intnl*, Article in Press (2010).

Forensic Science International xxx (2010) xxx–xxx

Contents lists available at ScienceDirect

Forensic Science International

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Screening for illicit drugs on Euro banknotes by LC–MS/MS

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ARTICLE INFO

Article history:
Received 14 April 2010
Received in revised form 19 July 2010
Accepted 28 July 2010
Available online xxx

Keywords:
Drugs of abuse
Paper currency
LC–MS/MS

ABSTRACT

A method for the simultaneous quantification of illicit drugs on Euro banknotes, using an ultra performance liquid chromatography tandem mass spectrometry, was developed and validated. The method included cocaine, benzoylecgonine, MDMA, MDEA, MDA, methamphetamine, diacetylmor phine, 6 MAM, morphine and Δ^9 THC. Drug residues were monitored and quantified via positive ESI mode using multiple reaction monitoring. Banknotes were extracted with methanol by vigorous shaking. Recovery rates were in the range of 60 80%. Calibration was performed with spiked banknotes in the range of 10 100 ng/note (R^2 0.98 0.99). Intra day analysis showed fair precision and accuracy (≤15%). Matrix effects were in the range from 27% to 235%. 7 15 samples of each denomination were analyzed. The calculated median values per note were 106 ng cocaine, 43 ng benzoylecgonine, 41 ng heroin, 15.5 ng 6 MAM, 16.5 ng morphine, 9 ng MDMA and 7 ng methamphetamine. Δ^9 THC was detected on 4 banknotes. MDEA and MDA were not detected on any note. A widespread background contamination for cocaine and opiates was demonstrated.

1. Introduction

Drug consumption has become a major societal problem in most countries as it is linked to high crime rates as well as other social disruptions [1]. According to estimations of the European Monitoring Centre for Drugs and Drug Addiction (EMCDDA), 22% of European adults in the age of 15 64 years have experience with the consumption of cannabis, 3 4% consumed at least once cocaine, ecstasy or amphetamine and about 1.2 and 1.5 million Europeans already consumed illicit opiates [2,3]. The world production for cocaine and opiates seems to be stable or is shrinking. However, the global problem with amphetamine type stimulants (ATS) is worsening [4,5]. Cannabis is still the most traded and seized herbal drug in Europe. In many countries across the globe, methamphetamine is reported to be the second most prevalent illicit drug after cannabis. Methamphetamine belongs to the ATS and is probably the most widely consumed synthetic stimulant in the world. Other prominent ATS are amphetamine and various “ectasy type” drugs (3,4 methylenedioxy N methyl am phetamine, MDMA and its close relatives 3,4 methylenedioxyam phetamine, MDA and 3,4 methylenedioxy N ethyl amphetamine MDEA) [6]. MDMA and cannabis are mainly used in compressed form (tablet or resin). Methamphetamine, cocaine and heroin occur in powder form in the market. Previous studies revealed the presence of significant amounts of various drugs, mainly cocaine, on different paper currencies [7 11]. Contamination may be caused by direct contact during drug consumption or trafficking. Drug ingestion by snorting via rolled banknotes leads to strong polluted paper currency. Large amounts of cocaine present on a single banknote could be spread to a very large number of other banknotes in general circulation. Drugs in compressed form are less likely to be retained by the fibers of banknotes than powdery drugs [12].

In many countries, currency suspected of being associated with drug trafficking can be seized by the authorities. One of the ways of investigating this association is through the analysis of seized banknotes for traces of illicit drugs [14]. If banknotes are used for evidentiary purposes, non invasive analyze method has to be applied to enable reanalysis by other laboratories. In this context, the application of Raman Microspectroscopy for the identification of drug crystals on paper currency is described. This method suffers from fluorescence interferences from cutting agents and is relatively insensitive in comparison to mass spectrometric methods, which are more commonly used for the identification and quantification of drugs on paper money [1]. Different analytical approaches (GC MS, LC MS, CE, GLORIA, IMS) were developed in the last years [15]. Thermal desorption tandem mass spectrometry (TD MS) is a very fast method and allows the analysis of 100 banknotes in a single 20 min analytical run [13]. The disadvantage of this method is that heating is (like rinsing of the banknote) a destructive process to the analyte (not to the banknote) so that analysis cannot be repeated [17]. Among the

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doi:10.1016/j.forsciint.2010.07.037

applied methods, LC MS was the most sensitive method with an LOD in the range of pg/note.

In this paper, a new validated method using ultra perform ance liquid chromatography triple quadrupole tandem mass spectrometry (UPLC MS) for the identification and quantifica tion of illicit drugs on Euro paper currency is presented. Attention is paid to the consideration of the matrix for drug quantification, which was disregarded in previous GC MS and LC MS studies. There is concern about the ability of analytical methods to distinguish between "dirty money", which has recently been in contact with drugs, and "background money", which has been in general circulation and may have been inadvertently contaminated [1]. Several illicit drugs are known to readily degrade in the presence of moisture (e.g. diacetyl morphine, THC) [17]. For a more precise picture of the grade of contamination and a better discrimination between "back ground" and "dirty" money, cocaine and heroin degradation products were analyzed. Banknotes were screened for cocaine, benzoylecgonine, heroin, 6 MAM, morphine, MDMA, MDEA, MDA, methamphetamine and Δ^9 THC.

2. Materials and methods

2.1. Chemicals and reagents

Water used in this study was deionized by a Millipore AFS 8 purification system and was >10 MΩ. Methanol and acetonitrile were of LC–MS grade. Glacial acetic acid (p. A. grade) was obtained by UCL. Ammonium acetate (ACS reagent grade) and formic acid (p. A. grade, 98–100%) were purchased from Merck. All drug standards were purchased from Cerillant. Cocaine hydrochloride, heroin, and 6-MAM (6-monoacetylmorphine) had a concentration of 1 mg/L in acetonitrile. Other drug standards had a concentration of 1 mg/L in methanol. Mini-UniPrep nylon filter (Whatman, 0.2 μm pore size) with polypropylene housing was used for filtration.

2.2. Banknotes

All banknotes (circulated as well as printfresh, non-circulated notes) were obtained from the National Bank of Luxembourg (Banque Centrale du Luxembourg, BCL). Notes were received in bundles of 10–20 notes, packed in plastic bags and originated from 8 different Euro emitting countries.

2.3. Extraction procedure

Euro banknotes were placed in a 50 ml glass vial to which 9 ml of methanol was added. The vial was sealed and shaken (300 min^{-1}) for 15 min. Extracts were transferred to a 10 ml glass vial and evaporated to dryness at 40 °C under a gentle nitrogen stream. Remaining residues were resuspended in 1 ml of a 80:20 mixture of ammonium acetate (5 mM, pH 4.5) and methanol. Extracted solids were removed by centrifugation (7 min, 14,000 rpm). A final filtration step with nylon filters was applied if extracted solids were not entirely removed by centrifugation. The supernatant was analyzed using the developed LC–MS/MS method. If necessary, samples were diluted with ammonium acetate/methanol 80:20 (5 mM, pH 4.5) to ensure a concentration in the calibration range.

2.4. UPLC conditions

Chromatographic equipment consisted of an Acquity ultra-performance liquid chromatography (UPLC) system (Waters, Zellik, Belgium). Separation was performed on an BEH C18 column (1.7 μm, 2.1 × 100, Waters). A multi-step linear gradient of solvent A (95:5 H_2O/acetonitrile + 0.5% formic acid) and solvent B (acetonitrile + 0.5% formic acid) was applied. The initial mobile phase contained 97.5% solvent A. The system was run in a linear gradient from 0.75 min to 4.25 min from 97.5% to 80% solvent A, followed by a gradient from 4.25 min to 4.50 min from 80% to 2.5% solvent A. A final linear increase to 99% of solvent A was performed from 5.50 min to 5.75 min. The total run time was 6 min. In all instances, the injection volume was 10 μl (full loop). Column temperature was set to 40 °C, sample temperature to 25 °C. Fig. 1 shows the seperation of a standard mixture.

2.5. MS/MS conditions

The LC system was coupled to a Waters Xevo TQ MS mass spectrometer with an atmospheric pressure electrospray interface. Waters MassLynx version 4.1 SCN 644

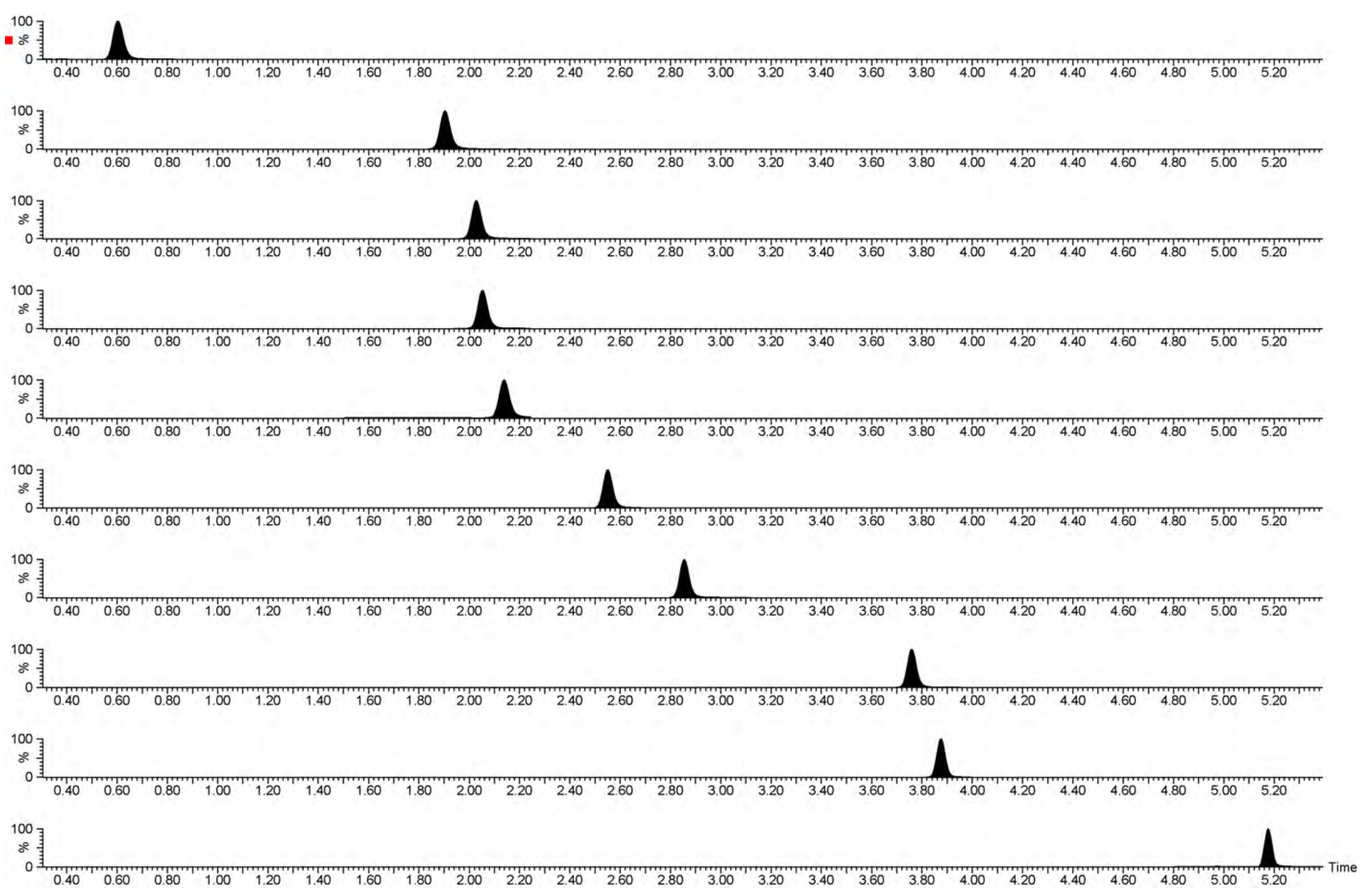

Fig. 1. Separation of a standard solution containing all analytes (100 ng ml^{-1}) applying a multi-step gradient (Acquity UPLC BEH C18 column, ESI^+ MS/MS detection). Peak identification from the top: morphine, MDA, methamphetamine, 6-MAM, MDMA, MDEA, benzoylecgonine, heroin, cocaine, Δ^9-THC.

Table 1
MS/MS parameter for the quantitative and qualitative daughter ions (*m*/*z*).

Analyte	Parent ion (*m*/*z*)	Quantative ion	Cone (V)	Collision (V)	Qualitative ion	Cone (V)	Collision (V)
Morphine	286.36	165.06	42	38	286.20	42	5
MDA	180.25	163.11	14	16	135.37	14	16
Methamphetamine	150.21	119.03	20	10	91.03	20	16
6-MAM	328.37	165.10	42	36	211.13	42	24
MDMA	194.27	135.39	20	19	163.07	20	12
MDEA	208.28	163.05	20	16	132.45	20	22
Benzoylecgonine	290.35	104.95	30	28	168.10	30	18
Heroin	370.38	165.11	44	50	268.18	44	26
Cocaine	304.37	182.11	32	18	82.04	32	30
Δ^9-THC	315.25	193.12	30	22	122.97	30	34

was used for LC–MS system control and data analysis. Analyte identification was performed by monitoring the protonated molecule with the two most intense product ions. The parameters used for the mass spectrometer under the ESI$^+$ mode were as follows: capillary voltage 3.00 kV, extractor voltage 3.00 V, source temperature 150 °C, desolvation temperature 650 °C, desolvation gas flow 1200 l h^{-1}, cone gas flow 30 l h^{-1}, collision gas flow (argon) 0.15 ml min^{-1}, collision cell pressure 3.22×10^{-3} mbar, LM1 2.8 V, LM2 2.8 V, HM1 14.5 V, HM2 14.5 V, ion energy 10.2 V, ion energy 20.8 V. Parameters for the cone and collision energy are listed in Table 1. Parameters optimization was done by MassLynx/IntelliStart. Drug residues were monitored and quantified using multiple reaction monitoring (MRM). Five time windows (0.4–0.7 min, 1.7–2.3 min, 2.3–3 min, 3.6–4.0 min, 5.1–5.4 min) were defined for MRM. Optimization of the mass spectrometer was performed by direct infusion of an aqueous solution containing all drugs investigated.

2.6. Method performance

Printfresh, non-circulating 5€ banknotes were used for the evaluation of the method performance data. A methanolic standard mixture containing all analytes with a concentration of 10 mg/L was prepared and stored at −70 °C. A six-point calibration in the range of 10–100 ng/note for all analytes (10, 20, 40, 60, 80, 100 ng/note) was performed. Banknotes were spiked with 10, 20, 40, 60, 80 or 100 μl of a diluted standard mixture (1 ng μl^{-1}). After a sufficient drying time (2–4 h), banknotes were treated according to the described extraction procedure. Linear regression with a $1/x$ weighting was performed. The limit of detection (LOD) and the limit of quantification (LOQ) were defined as, respectively, 3 and 6 times the level of noise. Intra- and inter-day analyses were performed each with five spiked 5€ banknotes (75 ng/note). The percentages of matrix effect (ME), the recovery of the extraction process (RE) and the overall process efficiency (PE) are calculated as: ME (%) = B/A × 100; RE (%) = C/B × 100; PE (%) = C/A × 100 [16]. A is the analyte peak area (75 ng ml^{-1}) in the resuspension medium ($n = 2$). B is the analyte peak area spiked into the resuspension medium (75 ng ml^{-1}) of 5€ blank extracts ($n = 2$). C is the analyte peak area in the resuspension medium of spiked (75 ng/note) 5€ notes ($n = 4$).

3. Results and discussion

3.1. Extraction procedure

Various extraction procedures are described in the literature applying acidification, different solvents and clean up processes [15]. Acetonitrile, methanol and chlorinated solvents were tested as extraction solvents. In all cases, a substantial amount of solids were extracted. In contrast to methanol, acetonitrile and chlorinated solvents also removed considerable amounts of colorants. An important consideration also is whether the method may destroy evidence of seized paper currency. Fingerprints on banknotes also may be valuable as money could be linked with an individual. Swabbing paper currency with methanol do not significantly affect fingerprint detection on banknotes [17]. Analyte reconstitution in a 80/20 mixture of ammonium acetate (5 mM, pH 4.5) and methanol was beneficial in concern of analyte stability and signal intensity.

3.2. Banknotes

A banknotes' serial number includes a letter that identifies the emitting country. Paper currency emitted by the Banque Centrale du Luxembourg (BCL) are/were printed in different European countries and show the identifier letter of the country, in which the money was printed. As a consequence, banknotes, emitted by the BCL, cannot be recognized as Luxemburgish notes. Analyzed banknotes originated from 8 Euro emitting countries.

3.3. Recovery and matrix effect

Very different recovery rates are reported for similar analytes by Bones et al. [7]. It was assumed that the basic nature of certain drugs of abuse may be responsible for a different extend of drug retention on banknotes. In fact, a possible matrix effect was not considered. Published data seem to correspond to values of the process efficiency (PE) which includes the matrix effect as well as the recovery of the extraction process. Moreover, banknotes, used for "recovery experiments", were prewashed with metha nol. This "cleaning step" definitely changes the matrix. Bank notes fell hard and firm [18]. Prewashed banknotes cannot be compared with untreated samples. Estee Turillas et al. [9] were performing two consecutive methanolic extraction steps of spiked banknotes. About 2% recovery in respect to the first extraction was reported for the second one. The absence of a matrix effect was concluded. We agree, that a second extraction

Table 2
Performance data: RE, recovery of the extraction process; ME, matrix effect; PE, process efficiency.

Analyte	R^2	LOD (pg/note)	LOQ (pg/note)	RE (%)	ME (%)	PE (%)
Cocaine	0.98	4	8	65 ± 7	235 ± 35	153
Benzoylecgonine	0.98	154	308	75 ± 2	61 ± 2	46
MDMA	0.96	746	1492	74 ± 7	113 ± 1.5	84
MDEA	0.98	114	228	68 ± 8	96 ± 9	65
MDA	0.99	158	316	65 ± 10	44 ± 3	29
Methamphetamine	0.96	10	20	79 ± 8	297 ± 25	235
Heroin	0.98	41	82	65 ± 6	30 ± 2	20
6-MAM	0.98	181	363	73 ± 3	69 ± 2	50
Morphine	0.99	216	432	70 ± 2	27 ± 0.3	19
Δ^9-THC	0.91	4762	9524	62 ± 18	37 ± 10	23

Please cite this article in press as: K. Wimmer, S. Schneider, Screening for illicit drugs on Euro banknotes by LC MS/MS, Forensic Sci. Int. (2010), doi:10.1016/j.forsciint.2010.07.037

Table 3
Performance data; intra- and inter-day analyses (75 ng analyte/note).

Analyte	Intra-day (n = 5)			Inter-day (n = 5)		
	Mean result (ng/note)	Precision (RSD, %)	Accuracy (error, %)	Mean result (ng/note)	Precision (RSD, %)	Accuracy (error, %)
Cocaine	71	7.2	5.4	67	13.1	10.3
Benzoylecgonine	72	3.6	4.7	74	13.3	1.2
MDMA	78	14.7	4.4	68	>20	9.2
MDEA	72	5.8	4.5	73	17.3	2.5
MDA	83	7.3	11.2	84	12.1	11.8
Methamphetamine	64	>20	14.0	58	>20	>20
Heroin	86	15.3	14.4	97	>20	>20
6-MAM	75	14.6	0.2	86	>20	13.9
Morphine	82	3.5	9.0	86	14.1	15.1
Δ^9-THC	94	11.2	>20	95	>20	>20

step does not improve the overall process efficiency. As already noted by Sleeman et al. [20], this does not necessarily exclude a matrix effect.

Evaluated performance data are listed in Table 2. Recovery rate and the matrix effect were evaluated with 5€ banknotes. The recovery rate for all analytes is in the range of 60 80%. Similar analytes showed very different matrix effects (cocaine: 235%; benzoylecgonine: 46%), leading to very different values for the process efficiency. If ME (%) = 100, no matrix effect is present. ME (%) > 100 represents a signal enhancement, ME (%) < 100% a signal suppression [16]. MDEA showed no significant matrix effect. A strong signal enhancement was observed for cocaine and methamphetamine. Other analytes were affected by signal suppression. As it is difficult to ensure a quantitative drug deposition on banknotes in particulate form, banknotes were spiked with drugs in solution. Sleeman et al. [20] raised concerns if the application of cocaine onto banknotes via solution adequately models the crystalline nature of cocaine observed on paper money as the contamination will most likely occur in particulate matter. The influence of the drug administration on paper money as solids or in solution remains to be investigated. Circulated banknotes are worn and show manifold contamination (dirt, finger grease, etc.). Non circulated banknotes were used in this study as contamina tions cannot be excluded for used and worn paper money. "Street" drugs usually also contain cutting agents and other impurities. These influences were not considered in this study. Signal enhancement may be the reason for the huge cocaine values reported in some studies [9].

3.4. Method performance

Many published studies for the analysis of drugs on paper currency do not report comprehensive method performance data. If performance data are published, no matrix consideration was made. To authors knowledge, this is the first study reporting a matrix effect for euro banknotes. Method performance data are presented in Tables 2 and 3. Calibration curves showed good linearity for all analytes (R^2 0.98 0.99), except methamphetamine and Δ^9 THC. Cocaine, benzoylecgonine, MDEA, MDA and morphine gave fair results for intra and inter day analyses. Values for MDMA, methamphetamine, heroin, 6 MAM and Δ^9 THC have to be regarded as semiquantitative, as inter day analysis showed deviations of over 20% for precision and/or accuracy. Results for THC and metham phetamine were calculated with a quadratic function. Fast hydrolysis is reported for THC and diacetylmorphine in the presence of moisture [12]. Banknote inhomogenities and different drying times after spiking also may influence analysis results.

3.5. Sample analysis

Numerous studies proved a widespread cocaine contamination of different paper currencies [15]. Moreover, the presence of cocaine, heroin, 6 MAM, morphine, methamphetamine, codeine, amphetamine and phencyclidine (PCP) on US paper currency is reported [11]. In addition, British pounds were tested positive for a range of narcotics, including cocaine, THC, MDMA, amphetamine and heroin [17,22]. Euro paper currency was screened before by a LC MS/MS method for a range of controlled drugs. Cocaine, benzoylecgonine and heroin contaminations are reported on Euro banknotes [7,9]. Very different cocaine contamination levels are published, ranging from beneath pg/note up to high μg amounts/note [7 9].

In the present study, 7 15 samples of each denomination were screened for drugs of abuse (in sum 64 banknotes). Non circulated 5€ banknotes were analyzed as blanks in each run. In order to get a better picture of the overall contamination per note, substances were grouped and summed up. Fig. 2 (cocaine, benzyolecgonine) and Fig. 3 (opiates: heroin, 6 MAM, morphine) show analyte group amounts/note, calculated for the free base form.

Cocaine was found on all samples analyzed. Banknotes contaminated with cocaine (COC) also showed significant amounts of benzoylecgonine (BE). A median amount/note of 106 ng (349 pmol) for COC and 43 ng (149 pmol) for BE was found. The presence of BE can be explained by the hydrolysis of cocaine on banknotes. Fig. 2 illustrates the sum of COC and BE in pmol/note. Two banknotes obviously exhibit higher contaminations. A 10€ note showed the highest cocaine deposits (12.4 μg COC, 4.2 μg BE, Σ55 nmol). These two samples showed 53 and 123 times the calculated median amount of 451 pmol/note (ΣCOC, BE). All remaining samples showed contaminations below 7 nmol for the sum of COC and BE. A study performed with Canadian banknotes indicated, that paper currency associated with criminal cases contained cocaine quantities that were 50 1000 times higher than those found on notes in general circulation [17]. Previous studies

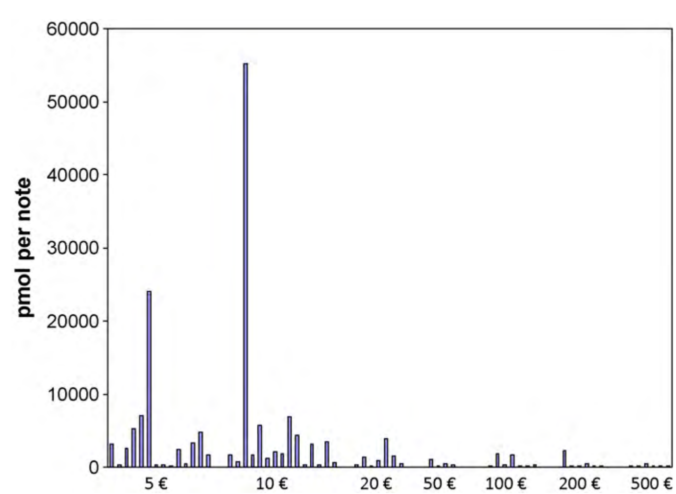

Fig. 2. Sum of cocaine and benzoylecgonine in pmol/note.

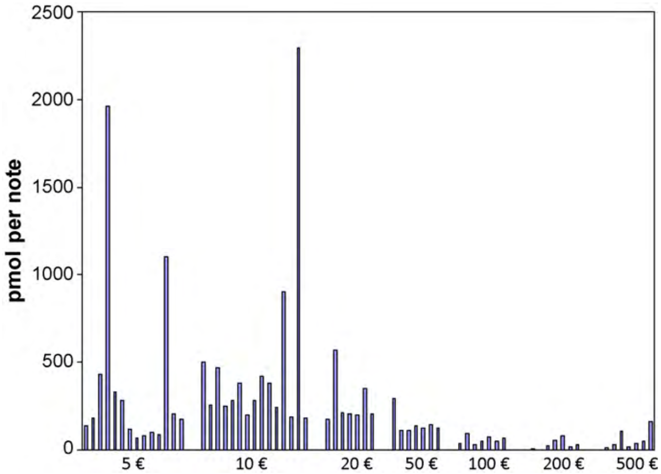

Fig. 3. Sum of opiates (heroin, 6-MAM, morphine) in pmol/note.

on Euro notes [7,9], using methanol and a similar extraction procedure, reported a small number of banknotes with definitely higher cocaine contaminations. The difference between ‘‘bank ground money’’ and ‘‘dirty money’’ may not be that huge for Euro banknotes than reported before for Canadian dollars. The significantly elevated cocaine levels of certain banknotes were correlated with a possible direct cocaine exposure during drug dealing or consumption. On basis of our results and by comparing with other similar Euro investigating approaches [7,9], we regard banknotes with contamination levels of under 7 nmol/note (ΣCOC, BE) as background money and those, exceeding this threshold, as suspicious of having been in direct cocaine contact.

Fig. 3 shows the sum of heroin, 6 MAM and morphine in pmol/note. Heroin and/or its degradation product 6 MAM were found on over 90% of all samples. 16 samples were tested positive for morphine, predominantly on 5€ banknotes. Four samples showed apparently higher opiate amounts. The highest opiate amount was detected on a 10€ note (507 ng heroin, 301 ng 6 MAM). Calculated median values per note were 41 ng (111 pmol) heroin, 15.5 ng (47 pmol) 6 MAM and 16.5 ng (58 pmol) morphine. Illicit heroin is rarely pure and may contain a number of other substances. Heroin particles were shown to exist over a wide range of size. Holt [19] calculated a median value for the size of heroin particles of 45 μm in diameter, which corresponds to 137 pmol (55.5 ng) and was proposed as a representative particle of illicit heroin. The majority of samples were contaminated with less than 500 pmol opiates (Σheroin, 6 MAM, morphine) per note with a median opiate sum of 160 pmol/note. The most contaminated banknote showed 14 times the calculated median amount. However, this seems to be not dissimilar enough to make a clear differentiation between ‘‘bankground’’ and ‘‘dirty’’ money. Assuming, that 6 MAM and morphine originate from hydrolysis of heroin on paper money, analyzed banknotes showed a median contamination of about one particle heroin per note. A poor transport between banknotes and a small percentage of banknotes in general circulation (approxi mately 2%) with traces of diacetylmorphine is described by Ebejer et al. [14,21]. However, our study showed a widespread opiate background on Euro banknotes.

53 notes showed traces of methamphetamine (median: 7 ng/note), whereas 80% of them showed quantities beneath 15 ng/note. Only 3 Euro notes showed levels over 100 ng methamphetamine/note. MDMA was found on 17 samples (median 9 ng/note), mainly on small denominations (5€, 10€, 20€). Bigger denomination almost showed no MDMA positive samples. The highest MDMA amount (115 ng) was found on a 10€ note. The less popular amphetamine type stimulants MDEA and MDA were not detected on any note. 4 banknotes were tested positive for traces of Δ^9 THC. One of which showed a high THC deposit (>3 μg/note).

In general, small denominations (5€, 10€, 20€) showed higher illicit drug amounts which can be correlated with their higher circulation rate and/or a more frequent use in street deals. Frequently used banknotes are more hackneyed. Their fibers spread apart and produce interstices that allow the inclusion of small particles [17]. Analyzed samples from small denomination had a much rawer surface than bigger denomination. In our opinion, this has a big influence on the grade of contamination. If results of banknotes analysis for traces of illicit substances should act as evidence, banknotes have to be distinguishable from banknotes with background contamination. For the evaluation of discrimination thresholds between ‘‘dirty’’ money and notes with background contaminations, possible degradation products should be taken into account.

4. Conclusions

A UPLC MS/MS method has been developed and validated for the determination of 10 illicit drugs of abuse on Euro paper currency. To authors knowledge, previous published LC MS as well as GC MS studies disregarded a matrix influence. In the present study, attention was paid to the matrix consideration using spiked non circulated Euro banknotes for the evaluation of performance data. All Euro denominations were tested. Small denominations (5€, 10€, 20€) showed higher drug quantities. Banknotes with considerable amounts of cocaine or heroin were also tested positive for their breakdown products. Euro banknotes are circulating in the European Union and other countries. Conse quently, geographical and sociological conclusions, as it was frequently done before [15], have to be regarded with scepticism.

Acknowledgements

Authors are grateful to the Fonds national de lutte contre le trafic des stupéfiants for financial support. Sincere thanks are given to the Banque Centrale du Luxembourg (BCL) for providing samples and for forthcoming collaboration.

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Attachment C15

Felix, J., and Gardner, E.A., Cocaine Contamination of Paper Currency in Birmingham, Alabama, *Proceedings Am. Acad. Forens. Sci.*, (2009).

ratio is relevant because it reflects the species of precursors and reagents used for the synthesis, the origin and synthetic method.

Usually, enantiomeric ratio of methamphetamine is measured using GC/MS method. Methamphetamine is converted to diastereoisomers with chiral derivatization reagents and separated by gas chromatography with a nonchiral column.

The best known derivatization reagents in literature: N (trifluoroacetyl)prolyl chloride (TPC) and (S) (+) α Methoxy α (trifluoromethyl)phenylacetic acid MTPA were used. The enantiomeric enrichment with D tartaric acid and subsequent derivatization with BSTFA with TMCS before analysis will be tried as well. The convenience, simplicity and speed of the different methods will be compared.

Methamphetamine, Enantiomer Ratio, Chiral Derivatization

A41 Cocaine Contamination of Paper Currency in Birmingham, Alabama

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After attending this presentation, attendes will have learned about analyte loss through different extraction methods. In addition, the methods can also be adapted and applied in any classroom setting to teach drug chemistry, techniques for extractions and GS/MS usage, and practical hands on experience with techniques applied in forensic laboratories. The long term aim of this project is to develop purification methods for profiling impurities and precursor materials.

This presentation will impact the forensic community by adding Birmingham, AL to the major U.S. cities that have been tested for the presence of cocaine in the local currency. In addition, the researcher will be able to analyze the pros and cons for dry extraction versus acid/base extraction methods, allowing analysts in forensic labs to choose between detection limit and injecting unknown impurities in sensitive lab equipment which may result in carry over to subsequent runs.

The objective of this project was to test $1 bills in Birmingham, AL for trace amounts of cocaine and to compare both purification of the sample and sample loss on a qualitative basis using a dry extraction and an acid base extraction for both cocaine on $1 bills and levmethamfetamine (l meth) in nasal decongestive inhalers. The attendee will learn about analyte loss through different extraction methods. In addition, the methods can also be adapted and applied in any classroom setting to teach drug chemistry, techniques for extractions and GS/MS usage, and practical hands on experience with techniques applied in forensic laboratories. The long term aim of this project is to develop purification methods for profiling impurities and precursor materials.

There have been numerous reports of the percentage of paper currency that is contaminated with cocaine and other controlled substances in both the U.S. and internationally. However, the term "dirty money," covers more than just the presence of a controlled substance. Contamination found on currency includes nicotine, bug repellent, sunscreen, Ritalin, procaine, plasticizers, cosmetics, glycerol, and other substances (JOEL). Potentially pathogenic bacteria were found on 94% of $1 dollar bills tested in west Ohio (Pope et al. 2002) and germs of fecal, respiratory, and skin origin were found on bills from Chicago, New York City, and Washington, DC (Turner 2001).

Twenty $1 bills randomly retrieved from a Wachovia bank in the Birmingham AL area were extracted with 10 ml of methanol. The methanol extract was divided into two equal portions and the methanol evaporated. One portion was then analyzed by dry extraction into $CHCl_3$ and the other portion underwent an acid base extraction. Results from GC/MS analysis of the extractions indicate that 80% of the bills were positive for cocaine when analyzed with the dry extraction, however, the chromatogram had many impurities. Some of the impurities carried over into the blank injected between each sample. The number of bills testing positive for cocaine was much less using the acid base extraction, however, the chromatograms were cleaner and there was no carryover.

Similar extraction experiments were performed using nasal decongestion Inhalers to compare the results of dry extraction versus acid/base extraction for l meth. Similar results were obtained: there was loss of the l meth after acid/base extraction relative to the dry extraction. The levels of some impurities were decreased relative to the l meth. There were some impurities that were not affected by the acid/base extraction and may, in fact, have even been enhanced. Carryover was not a problem in either of the extraction methods. This work is ongoing.

In conclusion, two methods were used to extract cocaine and l meth from $1 bills and Vicks decongestive inhalers, respectively. For both sets of date, the acid/base extraction results in a cleaner GC/MS spectrum, is better to run on the GC column, but yields less intensity in chromatogram peaks due to sample loss through the multi step cleaning process. Carryover of the impurities was seen in blank injections between cocaine sample runs.

Cocaine, Currency, Extraction

A42 Optimization of Solid Phase Micro Extraction - Gas Chromatography/Nitrogen Phosphorous Detector (SPME - GC/NPD) for the Detection of Methyl Centralite and Ethyl Centralite From Gun Shot Residues

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After attending this presentation, attendees will have had the opportunity to discuss a method for detecting small amounts of methyl centralite and ethyl centralite with a novel extraction scheme of using solid phase micro extraction. The ease of adaptation of this technique to forensic labs from other chemistry focused areas will be shown. Discussion of similar efforts towards advances in science being applied to forensics will be encouraged.

This presentation will impact the forensic community by explaining the many compounds that are specific to gun powder primers and stabilizers. For the purposes of uniqueness, methyl centralite and ethyl centralite were reported as highly significant to GSR. Detection of trace amount of methyl centralite and ethyl centralite has been a challenging task. This investigation of a novel extraction technique has created an alternative way to detect these GSR signature molecules. This new method will have a great impact on the determination of molecular marks of those GSR samples that couldn't be easily determined by conventional analytical procedures.

Methyl centralite (MC) and ethyl centralite (EC) are two signature molecules highly associated with gunshot residues (GSR). The objective of this work was to find a sensitive analytical method for extracting and identifying trace amount of EC and MC from GSR related samples.

A sensitive extraction scheme to extract MC and EC from the samples has been successfully developed, such as gun powders, un burnt gun powder residues collected near the target. The extraction was

Attachment C16

Sleemam, R., Burton, I.F.A., Carter, J.F., and Roberts, D.J., Rapid Screening of Banknotes for the Presence of Controlled Substances by Thermal Desorption Atmospheric Pressure Chemical Ionization Tandem Mass Spectrometry, *The Analyst*, **124** (1999).

The Analyst

Rapid screening of banknotes for the presence of controlled substances by thermal desorption atmospheric pressure chemical ionisation tandem mass spectrometry

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Received 4th November 1998, Accepted 21st December 1998

The ability to thermally desorb directly particulate matter, trapped on filter meshes, into the atmospheric pressure chemical ionisation source of a tandem mass spectrometer allowed the simultaneous detection of a range of controlled substances within complex matrices with a high degree of confidence. Dust samples were collected from bundles of banknotes using simple apparatus attached to a portable vacuum cleaner. This technique was employed without additional clean-up procedures, rendering the overall method extremely rapid. The intensities recorded for characteristic gas phase ion transitions allow the determination of the amounts of contaminants present. It has been reported that a significant proportion of bundles of banknotes are contaminated with cocaine. This study found that cocaine and heroin (and two related opiates) were present above the detection threshold on UK banknotes from general circulation. Differences in both the frequency and degree of contamination were apparent between bundles of banknotes from general circulation and those suspected of being associated with the trafficking of drugs. In addition, a significant number of bundles of banknotes, confiscated by H.M. Customs and Excise, were found to be contaminated with detectable levels of tetrahydrocannabinol and 3,4-methylenedioxymethylamphetamine.

Large quantities of controlled substances are seized by authorities within the UK each year. The transportation, repackaging, sale and use of such materials will almost inevitably cause contamination of the premises, clothing and other possessions of persons involved in these activities. In addition, dealing in controlled substances frequently involves the exchange of large sums of cash, which may in turn become contaminated. The presence of trace levels of controlled substances in premises and motor vehicles and on clothing and currency is frequently used as part of the evidence to establish a link between an individual and these substances. Furthermore, English law permits the seizure[1] of cash sums of £10 000 or more from persons suspected of being associated with drugs trafficking. A forfeiture order may subsequently be granted if this can be substantiated.[2]

The contamination of clothing, banknotes, *etc*., is assumed to result, at least in part, from microscopic particles of material, physically trapped between the fibres of the specimens. A strategy has therefore been devised whereby dust samples may be collected by means of vacuum sampling. Particles are collected on filter meshes using relatively simple equipment and are transferred to a laboratory for subsequent analysis. In this manner, it is not necessary for the items requiring examination to be physically transported to the laboratory. This methodology reduces the number of handling stages, which, in turn, minimises the possibility of inadvertent contamination from other sources; solvents, glassware, *etc*. A 'control blank' is also routinely taken in order to establish that the person involved in the collection of the sample and the equipment used are free from contamination with the compounds sought. The filter meshes are subsequently thermally desorbed in the laboratory, liberating volatile compounds into the atmospheric pressure chemical ionisation (APCI) source of a tandem mass spectrometer. A number of precursor–product ion transitions are monitored which are characteristic of specific compounds.

In this study, filters were analysed for the presence of the nine compounds listed in Table 1. A different range of compounds may be sought on each filter mesh as required. This technique has been applied to the detection of trace levels of explosives in extremely complex matrices, with no need for additional clean-up procedures.[3,4] It is evident that the removal and collection efficiency of the technique described will vary according to the chemical and physical nature of both the analyte and the substrate. The overall vacuum sampling strategy has been shown empirically to be suitable for the removal and collection of trace levels of a wide range of compounds, including the nine substances reported here, from a variety of substrates. The limits of detection of the overall approach are likely to differ from those achieved *via* alternative extraction procedures, such as those employed by other workers.[5,6] The rapidity of this approach enables a greater number of samples to be collected and analysed from a given population in the time available, an important consideration for forensic applications. Similarly, other potentially significant evidence, present in the form of soluble components, such as fingerprints and inks, is not destroyed. Although GC-MS is perhaps the most widely used confirmatory technique in analytical chemistry, Busch *et al.*[7] compared and contrasted it with MS-MS for the determination of targeted compounds in complex mixtures. They concluded that the analysis of targeted compounds (certain drugs) in the presence of complex mixtures (inks and dyes, finger grease and sweat, household contaminants and general dust and debris) is precisely the type of analysis for which MS-MS is suited.

A limited number of studies have examined the contamination of paper currency from North America with cocaine and related substances.[5,6] These two studies employed solvent

extraction to remove controlled substances from banknotes, followed by extensive clean-up procedures and GC–MS detection. Hudson[5] examined Bank of Canada notes in Regina, Saskatchewan. More recently, Oyler *et al*.[6] examined US dollar bills from various locations within the USA. They concluded that the contamination of banknotes with cocaine was widespread. Nevertheless, Hudson also concluded that although such contamination is commonplace, there may still be grounds to associate confiscated monies with the drugs trade if it is contaminated to an abnormally high degree.

The data shown illustrate the application of thermal desorption tandem mass spectrometry to the detection of nine controlled substances (Table 1) in dust collected from bundles of UK banknotes. Two groups of 97 and 96 bundles, each comprising approximately 250 banknotes, were analysed (a total of 48 250 banknotes). The first group[8] had been returned to the Bank of England Printing Works after a period in general circulation, ranging from 1 year for £5 notes to several years for £50 notes.[9] These were assumed to be representative of banknotes in general circulation at the time of this study, June 1995. The second group was typical of bundles of banknotes seized by H.M. Customs and Excise Officers within the UK between January 1994 and May 1996. At the time of seizure all these monies were suspected of being associated with the trafficking of controlled substances.

Experimental

Equipment

Each dust sample was collected using a specially designed disposable brush-head cartridge assembly (DBCA), fabricated from stiff card [Fig. 1(a)] (S. H. Fiske, Bristol, UK). The opening at the front of the DBCA supports a row of bristles, designed to liberate dust from the object being sampled. The body of the DBCA holds a filter cartridge [Fig. 1(b)] which supports three quartz mesh elements designed to collect particulate matter and adsorb vapours. The mesh elements are coated with dicyanoallylsilicone gum (OV-275) to enhance collection efficiency. When used correctly, it is not possible for the operator to come into contact with these meshes. In operation, the DBCA is mounted on the nozzle of a portable domestic vacuum cleaner. Particle laden air is then drawn through the DBCA by the vacuum cleaner, which is located upstream with regard to the direction of air flow and is, therefore, unlikely to contaminate the filters. The filter cartridges are manufactured with a locating key on one face, ensuring that dust is collected on only one side of the meshes. When the meshes are desorbed, air passes through in the same direction, reducing the amount of particulate material carried to the ion source of the mass spectrometer. For routine applications, the DBCA is supplied in a heat-sealed plastic bag together with a tamper-evident bag into which it is sealed for return to the laboratory.

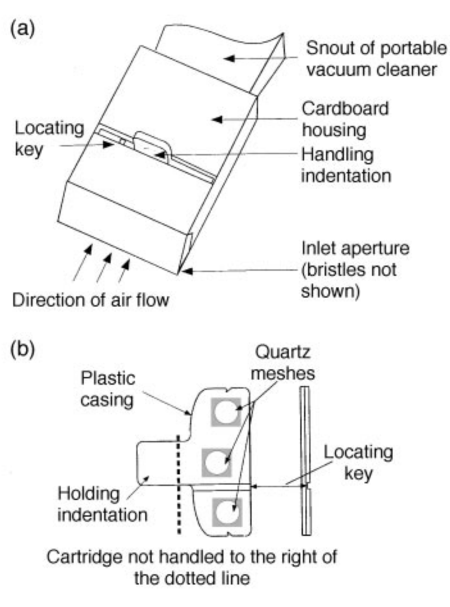

Fig. 1 (a) Disposable brush-head cartridge assembly (DBCA) with filter cartridge installed, shown fitted to a portable domestic vacuum cleaner, as employed during sample collection. (b) Filter cartridge assembly.

Sampling

Dust samples were collected at the Bank of England Printing Works (Loughton, Essex, UK) using an Electrolux Harmony 1300 W variable speed domestic vacuum cleaner equipped with a DBCA unit. The vacuum cleaner was adjusted to produce an air flow of 2.5 m s^{-1}, measured at the head of the DBCA unit with a cartridge installed. The flow was calibrated using an Airflow Instrumentation TA2 anemometer/thermometer (Airflow Developments, High Wycombe, Bucks., UK).

Wearing a disposable paper oversuit and gloves, the operator covered a table with a layer of clean aluminium foil. A DBCA was fitted to the vacuum cleaner and passed over the entire surface of the foil and the operator's gloves. The sample thus obtained was designated as a control blank. The bundles sampled were drawn from larger bundles which comprised 500 individual UK banknotes, which had been returned to the Bank of England in sealed, labelled, plastic wrappers, indicating the date and the location of source. A Bank of England employee separated approximately 250 notes from a bundle and handed these to the operator for sampling. The Bank of England staff were requested to handle the cash in as normal a manner as possible and took no unusual precautions to preclude cross-contamination. It was thought that this would best reflect the conditions under which cash sums are normally handled. Particulate matter was collected from the bundle of banknotes by holding it above the aluminium foil covered surface, fanning the banknotes out and passing the DBCA over the money and the foil surface so that any particles disturbed from the notes were drawn on to the filter meshes. The sampling time was of the order of 30 s. The bundle of banknotes was then handed back to the Bank of England employee and the surface of the aluminium foil again vacuumed. The cartridge was removed and sealed into a suitably labelled plastic bag. The aluminium foil, gloves and filter holder were discarded. A total of 97 bundles, comprising approximately 25 000 individual banknotes, were analysed in this manner.

Dust samples from monies seized by H.M. Customs and Excise were collected by trained Customs Officers spanning the period January 1994 to May 1996. Officers responsible for collecting the samples were instructed to use the above procedures. Samples were collected using a hand held portable vacuum cleaner (Black and Decker HC150), which produced a similar air flow to the system used at the Bank of England. The sample size and collection procedure were, therefore, comparable to those employed at the Bank of England.

Mass spectrometry

The analytical instrument used for this study was an Aromic 9100 triple quadrupole mass spectrometer (Perkin-Elmer SCIEX, Thornhill, ON, Canada) specifically designed for sample introduction by thermal desorption and APCI. The instrument was tuned using diisopropyl methylphosphonate

vapour bled into the ion source in a flow of high purity air (99.999%) (BOC, London, UK) and ionised in the positive mode. A number of reference peaks were monitored across the mass range using each of the analysing quadrupoles and the resolution was adjusted to give half-height peak widths of between 0.64 and 0.70 Da at *m/z* 29 and between 0.74 and 0.80 Da at *m/z* 361. Mass calibration was effected using these ions and the ion at *m/z* 181. Finally, the electron multiplier voltage was adjusted for optimum response to the ion at *m/z* 361. A system check was then performed which monitored the response of the instrument to a 1 μl aliquot of a standard solution containing cocaine (1 ng), diacetylmorphine (heroin) (2.5 ng) and Δ^9-tetrahydrocannabinol (THC) (1 ng). Mass calibration, peak width adjustment and system performance checks were conducted at the beginning and end of each day's operations and were automatically prompted following 4 h of operation.

The filters were removed from their packaging and inserted into the analytical instrument by the operator without the need for any further handling steps. The relevant control blank was analysed immediately prior to each sample. Control blanks and sample cartridges were treated in an identical manner. The operator entered the identity of the sample into the data system, all subsequent operations being automated. The filter cartridge was positioned so as to align with the stream of high purity air at a flow rate of 2 l min^{-1}. A small element heated the air stream to a temperature of 330 ± 30 °C (measured immediately after the heated element) by application of a 5.0 A current for 2.0 s, followed by 6.0 A for a further 13 s. The temperature achieved varied according to the amount of dust present on the cartridges, which may have restricted the flow of air. The desorbed vapours were entrained in this stream and carried along a PTFE lined transfer tube, maintained at a temperature of 200 °C, to the ionisation source of the mass spectrometer. APCI was used with the corona discharge current maintained at 3 μA (corresponding to about 6 kV). Ions were introduced to the mass analyser region *via* a 250 μm orifice. Dry nitrogen curtain gas was passed across this opening to prevent the ingress of atmospheric impurities and to facilitate the break-up of adduct ions.[10]

Filters were screened for the presence of the nine compounds listed in Table 1. The instrument was used in the multiple reaction monitoring (MRM) mode, sequentially scanning 21 transitions for 20 ms each, for a total time of 15 s. The collision region was operated with argon at a concentration of 300 mmol cm^{-3} and an offset voltage of 58 V for heroin and methaqualone and 41 V for all other compounds. Ion counts for each transition were recorded approximately 26 times throughout the desorption process, data being acquired and processed using the Aromic data system operating on a Digital PDP/11 computer. Data reported show the peak height of the transient signal recorded for each transition during the desorption process.

Routinely, two of the filter meshes were analysed for the presence of a range of compounds. The third mesh was retained for possible subsequent analysis either by this or some other complementary technique. Although thermal desorption is considered to be a 'destructive' technique, it has been shown empirically that the process does not remove all material and further analyses may be performed on any of the meshes.

Following each sample in which the presence of a monitored substance was detected, a purge cycle was initiated by the operator. This procedure entailed the introduction of an aluminium block with the same profile as a filter cartridge into the instrument. A sequence was then initiated whereby hot air (about 380 °C) was passed through the desorption region and heated transfer line for 15 s at each mesh position, to remove residual contamination. This was automatically followed by a normal analytical sequence with the aluminium block *in situ*. The purge cycle was repeated until the signals recorded returned to below established values. Two unused cartridges were then analysed and found to be blank before proceeding with any further analyses.

Results and discussion

The APCI mass spectra of the nine substances examined are dominated by the protonated molecule, $[M + H]^+$. These spectra provide little information other than confirming the molecular mass of the compound. In contrast, the product ion spectra of these protonated species, shown in Fig. 2, are highly specific to the compounds of interest. In the analytical methodology adopted, a complete product ion spectrum is not recorded, and the mass spectrometer dwells for a longer period on gas phase transitions which have been empirically found to be highly specific to the compounds of interest, not necessarily the most intense transitions. In this way, an enhancement in sensitivity is obtained without a concomitant loss in selectivity. For most compounds only two precursor–product transitions are monitored, although simple molecular species require more than two transitions to be recorded for positive identification.[3] Similarly, the very high detection threshold designated for the precursor–product transition *m/z* 136→119 (150 000 ion counts) reflects the lower specificity to amphetamine. It must also be noted that the transitions corresponding to THC are characteristic of Δ^9-tetrahydrocannabinol, Δ^8-tetrahydrocannabinol and certain other cannabinoids which are natural constituents of cannabis.

The signal thresholds, shown in Table 1, were established empirically for each of the chosen precursor–product transitions and represent detection limits in excess of three standard deviations above the average signal observed from many thousands of analyses performed on dust samples collected from a wide range of substrates over a period of many years. For a compound to be positively identified, the response obtained from all relevant precursor–product transitions must be above the threshold levels. If the response for any of the ion transitions monitored was below the threshold, the compound was deemed not to be detected. The ratios of the ion transitions were also required to lie within a range of 0.5–2 times those recorded for an authenticated standard for positive identification. A simple criterion to confirm the presence of a compound was thus established.

Results from the analysis of samples and control blanks collected by H.M. Customs and Excise and from the Bank of England were treated as four discrete data sets. For each data set the average and standard deviation of the peak height for each precursor–product transition were calculated. These results were then used to calculate the range of signal (calculated as average ± 1.96 × standard error of measurement) expected for each transition at a 95% level of confidence,[11] shown in Table 1. The signals recorded, corresponding to cocaine, THC, heroin, MDMA and amphetamine for each sample from both groups, are shown graphically in Fig. 3. For clarity, Fig. 3 shows only the intensity of the first transition listed in Table 1, data for other transitions being in close agreement. Narcotine and papaverine, which are products of the opium poppy, were found to occur with heroin and are not included in Fig. 3, also for clarity. The range for the percentage of bundles of banknotes which exceeded the detection threshold for specific compounds, at a confidence level of 95% (calculated as $P \pm 1.96 \times$ standard error of percentage),[12] is given in Table 2. Only data from the analysis of the central filter meshes are shown in Fig. 3 and Table 2. Data from the analysis of the second mesh of each cartridge were in close agreement with results from the first mesh and are not presented for clarity.

No controlled substances were detected on any of the control blank cartridges acquired at the Bank of England. The signals recorded were equivalent to approximately 20 pg of cocaine and 100 pg of other compounds, but these were all below the designated thresholds. There was no statistical difference

between the range of signals recorded for the control blanks taken from the Bank of England and those collected by H.M. Customs and Excise corresponding to any of the compounds sought. This indicates that the environments in which both groups of samples were collected could be considered to be free from contamination with these compounds. Two control blank cartridges acquired by H.M. Customs and Excise showed small, but detectable, responses for cocaine (equivalent to approximately 60 and 80 pg). This was probably due to contamination from paper oversuits which are not routinely changed between the collection of different samples. In practice, data from the samples corresponding to these control blanks would be considered unreliable but are included for the purpose of this study. With these two exceptions, all control blanks yielded signals far below the designated thresholds.

Cocaine, heroin, narcotine and papaverine were all deemed to be present on at least one of the bundles of banknotes sampled at the Bank of England. Of these compounds, only the signal ranges for the precursor–product transitions corresponding to cocaine were statistically different from the control blanks at a 95% confidence level, probably because the opiates were only detected on a single sample. The upper range of signal recorded for cocaine was equivalent to approximately 1.1 ng. Of the 97 bundles of banknotes sampled, 39 were deemed to be contaminated with cocaine, which was equivalent to 40.2% of the samples. Assuming that the number of banknotes in general circulation represents an infinitely large population, it may be inferred that there is at least a 31.4% chance of a bundle of 250 banknotes drawn from general circulation being detectably contaminated with cocaine. These data show a slight trend for

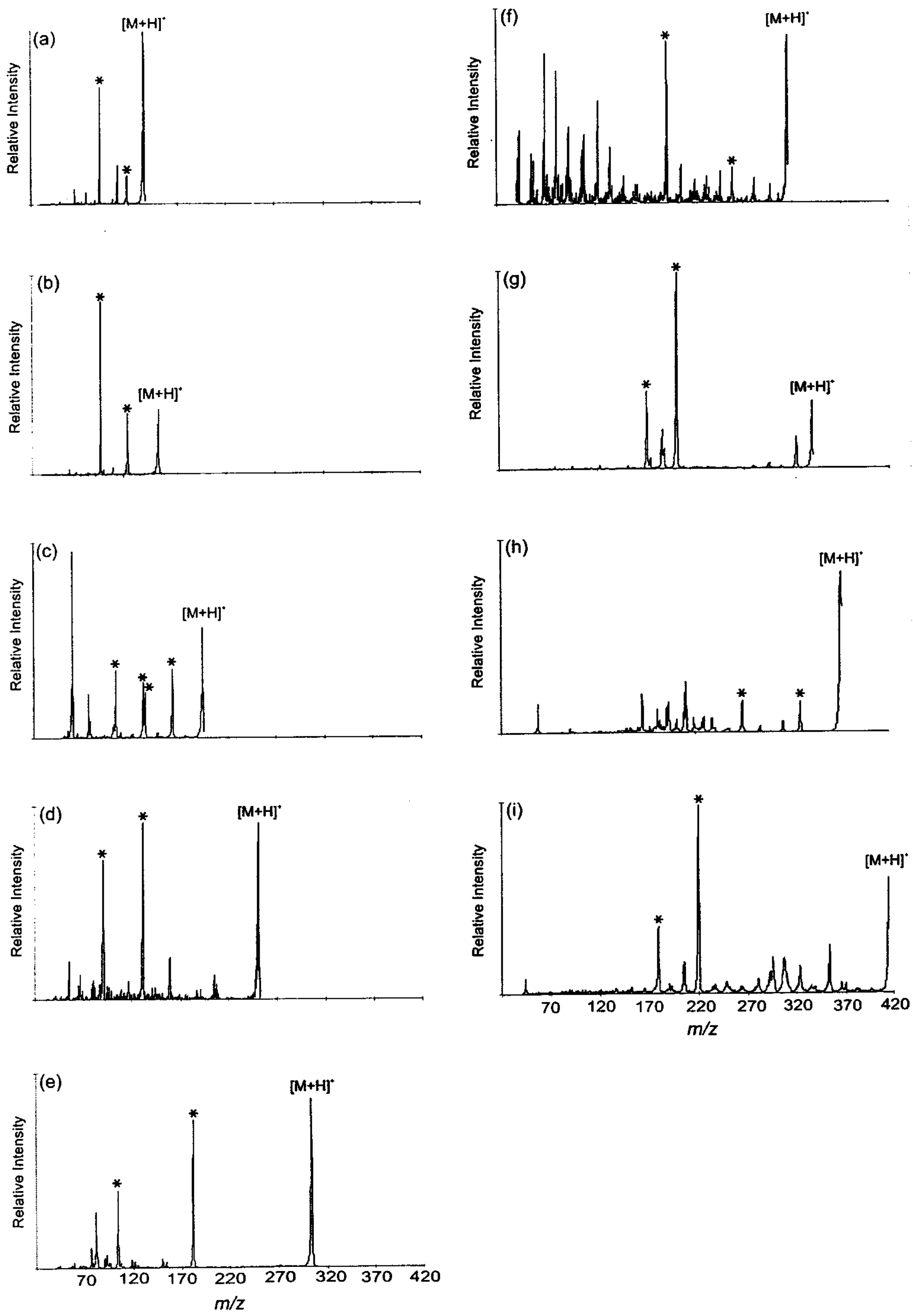

Fig. 2 Product ion mass spectra of (a) amphetamine, (b) methamphetamine, (c) MDMA, (d) methaqualone, (e) cocaine, (f) THC, (g) papaverine, (h) heroin and (i) narcotine, showing $[M + H]^+$ species formed by atmospheric pressure chemical ionisation and monitored product ions (marked with asterisks).

smaller denominations to be more frequently contaminated, £5 (57%), £10 (42%), £20 (37%) and £50 (19%), possibly reflecting a higher incidence of contact between these denominations and cocaine or the greater number of transactions which these denominations undergo. A single bundle of £5 banknotes exceeded the detection limit for heroin, equivalent to approximately 500 pg. The same bundle also contained traces of narcotine and papaverine, which are natural products of the opium poppy [*Papaver somniferum* L. (Papaveraceae)]. Despite this finding, ranges of both the signal level and percentage contamination, at 95% confidence, were not significantly different from the corresponding control blanks. These data, therefore, do not provide conclusive evidence that any proportion of UK banknotes in general circulation is contaminated with opiates. The detection of high frequencies or amounts of heroin contamination can, therefore, be viewed as uncommon.

The extent of contamination found on bundles of banknotes confiscated by H.M. Customs and Excise was more intense and widespread than found on those sampled from general circulation, as is apparent from Fig. 3. Cocaine, THC, heroin, papaverine, narcotine, amphetamine and MDMA were all positively identified on at least one bundle of banknotes. With the exception of amphetamine and THC, the ranges of signal intensities recorded were all significantly greater than those from the corresponding control blanks. In addition, the ranges of both signal intensity and percentage contamination for cocaine, heroin, narcotine, papaverine and MDMA were significantly greater than those recorded from banknotes in general circulation. The differences in both the frequency and intensity of contamination with cocaine between confiscated banknotes and those in general circulation were less distinct than observed for other compounds and were not distinct at a 95% confidence level (Tables 1 and 2). The upper range of the signal corresponding to cocaine on confiscated banknotes was equivalent to approximately 2.9 ng. Many of the bundles of seized banknotes analysed were, however, contaminated with such large amounts of cocaine that the response of the detector was saturated. This was also obvious from the number of purge cycles required to remove all traces of the compound from the instrument following the analysis of dust from a number of bundles of confiscated banknotes. A more distinct difference between the two populations would undoubtedly have been apparent had the dynamic range of the analyser been greater. It is also unquestionable that the frequency of contamination observed is dependent on the designated detection threshold and it is essential, therefore, that comparisons are made only between samples acquired and analysed in an identical manner. Had a higher detection threshold been assigned, the percentage of bundles of confiscated banknotes deemed to be contaminated with cocaine would have been much greater than those from general circulation.

The range of signals recorded corresponding to, methaqualone, methamphetamine and amphetamine from the Bank of England and H.M. Customs and Excise samples were not statistically different from each other, or from the corresponding control blanks. Methaqualone and methamphetamine were not positively detected on any of the samples analysed. Amphetamine was detected above the threshold level on a single sample collected by H.M. Customs and Excise with the outcome that the signals recorded encompassed a wide range, including zero. This is consistent with the range of the proportion of samples found to be contaminated, which also includes zero, indicating that the detection of amphetamine, methamphetamine or methaqualone on bundles of banknotes is, again, far from commonplace.

Estimates of the levels of controlled substances detected have been made by comparison with the response obtained from the standard solutions analysed during the system checks. Material deposited from solution has, however, been empirically shown to exhibit a much sharper desorption profile than material collected as part of a dust sample. Also, the total amount of material collected on a filter mesh will affect the efficiency of the APCI process and may reduce the response of the instrument to any targeted substances present. Using this comparison, the

Table 1 (i) Target compounds, (ii) gas phase ion transitions recorded, (iii) designated detection threshold for each transition and (iv) range of ion counts predicted for each transition, at 95% confidence (unless stated otherwise)

			(iv)							
			Bank of England control blanks (ion counts)		H.M. Customs and Excise control blanks (ion counts)		Bank of England samples (ion counts)		H.M. Customs and Excise samples (ion counts)	
(i) Compound	(ii) Precursor→ product (m/z)	(iii) Detection threshold (ion counts)	Lower	Upper	Lower	Upper	Lower	Upper	Lower	Upper
Cocaine	304→182	30000	4318	5627	5173	8963	123810	440411	519906	1134886
	304→105	20000	2105	2616	2859	4391	43928	117091	268264	741935
Cocaine	304→182	30000	4111	5834	4574	9563	65954	491548	422639	1232154
at 99% confidence	304→105	20000	2024	2697	2617	4633	18659	228961	193347	816852
THC[a]	315→193	13500	703	1232	1232	1984	485	663	7478	24945
	315→259	4500	651	744	798	1056	615	662	1639	4251
Heroin	370→328	3000	186	214	183	726	0	652	1746	9548
	370→268	3000	340	378	884	1638	72	679	1364	6441
Papaverine[b]	340→202	6000	471	535	337	798	441	825	1384	5184
	340→171	3000	741	890	768	1018	676	756	1001	1842
Narcotine[b]	414→220	12000	489	584	329	400	0	6072	13053	49544
	414→179	12000	2106	2508	1705	2126	1588	2671	3323	7268
Methaqualone	251→132	30000	1524	1819	1201	1799	1703	2087	1289	1931
	251→91	30000	2061	2216	3495	4196	2490	2652	3712	4591
Methamphetamine	150→119	20000	866	981	1045	1363	851	898	1055	1826
	150→91	80000	4678	5212	5008	5922	4617	4833	5858	10498
	150→32	30000	358	437	203	258	389	424	376	667
Amphetamine	136→119	150000	4350	5051	4744	7056	3689	3977	3125	16682
	136→91	50000	7200	7724	11032	13393	7482	7768	0	69424
MDMA[c]	194→163	10000	557	611	478	598	636	682	2980	32794
	194→135	10000	2864	3018	1746	2951	2865	2945	4037	21600
	194→133	10000	1180	1273	1034	1344	1390	1496	3072	25001
	194→105	10000	1231	1326	1132	1433	1423	1506	3576	30096

[a] Tetrahydrocannabinol, the active constituent of cannabis. [b] Natural products of the opium poppy. [c] 3,4-Methylenedioxymethylamphetamine or 'ecstasy'.

Table 2 Confidence interval for proportion of bundles of banknotes found to be contaminated, at 95% confidence (unless stated otherwise)

Compound	Bank of England control blanks (%)		H.M. Customs and Excise control blanks (%)		Bank of England samples (%)		H.M. Customs and Excise samples (%)	
Cocaine	0.0	0.0	0.0	4.9	31.4	51.0	56.1	75.1
Cocaine at 99% confidence	0.0	0.0	0.0	5.8	28.3	54.1	53.1	78.1
THC	0.0	0.0	0.0	0.0	0.0	0.0	7.5	21.6
Heroin	0.0	0.0	0.0	0.0	0.0	3.0	9.2	24.1
Papaverine	0.0	0.0	0.0	0.0	0.0	3.0	0.2	8.2
Narcotine	0.0	0.0	0.0	0.0	0.0	3.0	8.4	22.9
Methaqualone	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Methamphetamine	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Amphetamine	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.1
MDMA	0.0	0.0	0.0	0.0	0.0	0.0	3.5	15.2

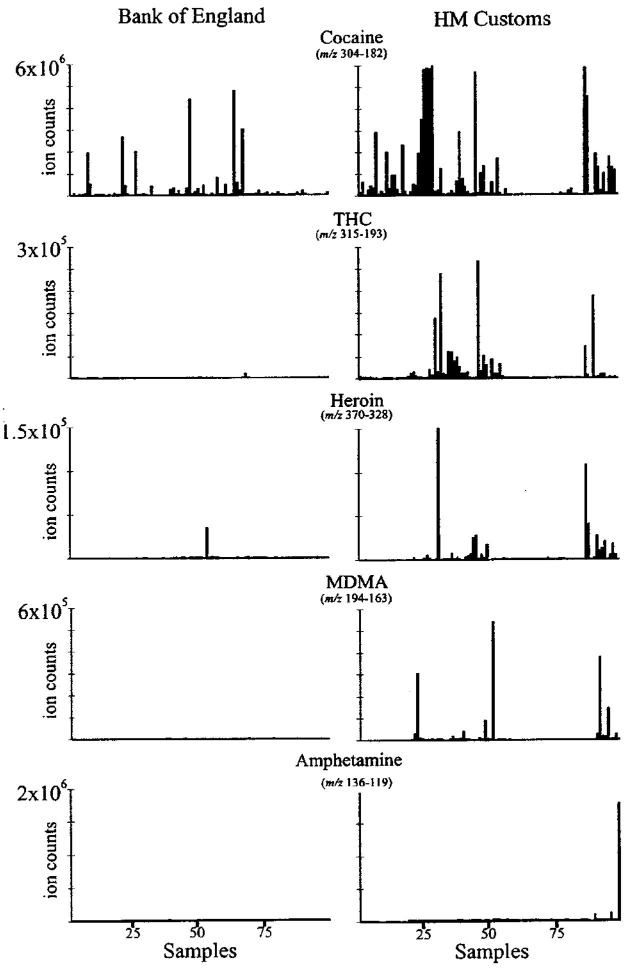

Fig. 3 Bar charts showing the response recorded for each sample, corresponding to five compounds, of the two banknote groups studied.

responses obtained from the six most heavily contaminated bundles of banknotes from the Bank of England indicate that the level of contamination collected on the filters was in excess of 5 ng of cocaine per bundle. Other contaminated bundles yielded at least 100 pg. Since each bundle contained approximately 250 banknotes, it is impossible to ascertain whether the contamination observed was distributed evenly amongst the banknotes or concentrated on a few individual specimens. It is also certain that the sampling procedure did not remove all the material present on the bundles of banknotes. In addition, it is not possible to estimate the proportion of material removed and, therefore, attempts to quantify the levels of controlled substances present on either the bundles or the individual notes are further complicated. Despite these restrictions, the technique does provide an indication of the overall concentration of controlled substances present on the bundles of banknotes and, therefore, may provide valuable evidence of contact with these compounds.

The data reported in this study are similar to the findings of both Hudson[5] and Oyler *et al.*[6] as a significant number of bundles of UK paper currency examined from general circulation were found to be contaminated with cocaine. The levels of contamination detected were significantly lower than those reported by Oyler *et al.*,[6] possibly reflecting different sampling procedures or different geographical patterns of drug use. These data also confirm the findings of Hudson[5] that the levels of cocaine contamination on bundles of banknotes alleged to be associated with the trafficking of controlled substances are significantly higher than those observed on bundles of banknotes in general circulation. In addition, this study has shown that the occurrence of controlled substances, other than cocaine, on bundles of UK banknotes in general circulation was rare, in contrast to those suspected of being associated with the trafficking of such substances. The rapidity of the overall technique described allows sufficient samples to be collected and analysed in a given period for valid comparisons to be effected.

Acknowledgements

The authors thank the Bank of England and H.M. Customs and Excise National Investigation Service, Manchester for their cooperation in the collection of the samples for this study. Perkin-Elmer SCIEX, Canada, are thanked for their collaboration with instrument development. Pete Waller, Dave Leggett and S. H. Fiske Ltd. are acknowledged for their work in the development of the DBCA.

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Paper 8/08573K

Attachment C17

Sleemam, R., Burton, I.F.A., Carter, J.F., Roberts, D.J., and Hulmston, P., Drugs on Money, *Anal. Chem*, June (2000)

DRUGS ON MONEY

A U.S. government report revealed that in 1995, an estimated 3.3 million U.S. citizens were designated hardcore cocaine users, annually consuming between 287 and 376 metric tons of cocaine at a cost of $38 billion USD (U.S. dollars) (*1*). In the same year, Americans spent $57 billion USD on illegal drugs, compared with $43 billion USD on tobacco products (*1*). Drug use is known to foster crime; increase the spread of health problems such as hepatitis, heart disease, and AIDS; and disrupt personal, family, and legitimate economic relationships.

The public bears the costs of this high level of drug consumption through the funding of the criminal justice system, drug treatment programs, and anti-drug programs. In an effort to combat the trade in illicit drugs, many countries have introduced laws that permit the seizure of money associated with drug trafficking. The detection of trace quantities of controlled substances (e.g., cocaine, diacetylmorphine, Δ^9-tetrahydrocannabinol [THC], and amphetamine-related compounds) on banknotes is frequently used as part of the evidence to obtain a forfeiture order for suspected drug dealers.

Even if the analyst can establish the presence of controlled substances on banknotes, this does not automatically imply a direct link with the use or trafficking of that compound. Several studies have demonstrated that a significant number of U.K. and North American banknotes in general circulation carry traces of cocaine (*2–4*), and we have detected other illicit compounds on banknotes. These findings should not be surprising, because these commodities are traded using cash, which is handled by the same fingers that directly touch the drugs or wrappings. The crucial question for law enforcement agencies is whether "drug money" can be differentiated from money in general circulation.

Demonstrating the presence of substances of abuse is only one facet of the forensic evidence that may be obtained from a particular exhibit. Fingerprint evidence, for example, also may be valuable. Linking money with a drug or drugs may only be significant if the money also can be linked with an individual. An important consideration is whether the analytical method may destroy other valuable evidence. Surprisingly, empirical evidence has shown that methods that involve swabbing with methanol or direct heating do not significantly affect fingerprint detection on banknotes.

Several mechanisms have been postulated for the retention of controlled substances by banknotes. It has been suggested, for example, that the ink on currency never really dries and, therefore, provides a microscopic, sticky surface onto which human oils and miscellaneous environmental dirt and grime (including narcotics) can become

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In the war on illegal drugs, it is important to distinguish "drug" money from "innocent" money.

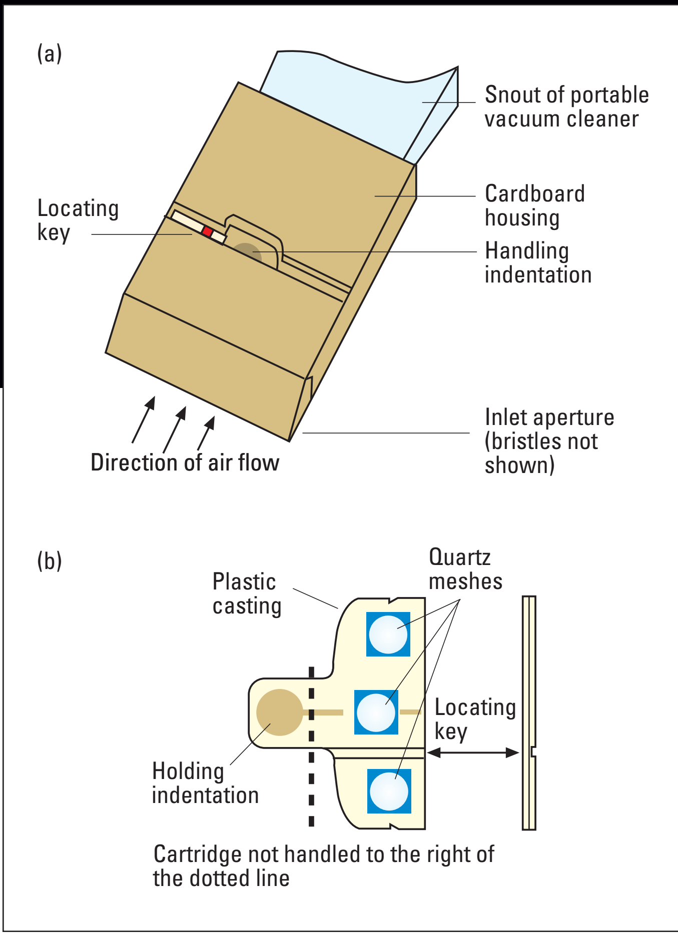


FIGURE 1. (a) Vacuum and (b) vacuum head for collecting dust at a crime scene.

attached (*5*). Other data have shown that after a period of use, the fibers of banknotes spread apart to produce interstices that allow the inclusion of small particles (*6*). Further, the cotton–linen fibers used to manufacture banknotes may bind chemically with controlled substances and become a significant retention mechanism. The surface and body of banknotes typically contain high amounts of innocuous substances, such as ink, finger grease, cosmetics, and dust particles (*7*), while traces of controlled substances are rarely present in more than nanogram quantities. Any practical analytical method must, therefore, be extremely sensitive and have a very high degree of selectivity for the compounds of interest (*7*).

A U.S. court has ruled that evidence of banknotes contaminated with drugs is not admissible unless it can be demonstrated that the traces are markedly different from those that would be expected on banknotes from a particular geographical area (*8*). One study cited in the ruling included evidence that >75% of all circulating currency in Los Angeles is contaminated with residues of cocaine or other controlled substances. Several related studies suggest that contamination is widespread and traces are easily transferred. In an experiment in which eight samples of cash were taken from civic dignitaries in Orlando, Florida, six out of the eight samples showed detectable amounts of cocaine (8).

Drug collection, detection, and analysis

Possibly the best device for locating minute traces of controlled substances within a large search area is a dog. A trained dog can walk through a residence and complete a search of all the articles present, including banknotes, within a few minutes (*5, 9*). In contrast, hundreds of samples might be needed to ensure a complete search using an instrumental technique. Though dogs can indicate the presence of vapors associated with certain substances, it remains the work of forensic scientists to specify the types and quantities. Courts have only recently explored the possibility of admitting "canine evidence"—a skilled handler's interpretation of a canine response (*7*).

Banknotes can be sampled in batches or individually. In choosing an approach, an investigator must consider the overall quantity of banknotes and the techniques available. Various methods have been used for the removal of material from banknotes, including vacuum sampling, solvent extraction, and direct thermal desorption.

Portable, domestic vacuum cleaners are now widely used to collect dust samples at crime scenes (Figure 1) (*10*). Material can be collected from any dry surface onto a small filter held at the end of a vacuum cleaner hose. Because air does not pass through the vacuum cleaner before reaching the filter, any compounds identified on the filter can be assumed to have come from the object being examined. This technique does not require portable analytical equipment or that the objects being examined be physically transported to the laboratory, thus reducing the amount of handling and the possibility of contamination. Efficiency of the collection and analytical procedures will vary for different substances, matrixes, and substrates, and the technique is best regarded as semiquantitative. Vacuum techniques allow remote sampling and the sampling of relatively large amounts of cash with a single filter. The low efficiency of removal generally renders the approach unsuitable for analyzing individual notes. Traces of controlled substances on the filter can be detected using immunoassay, ion mobility spectrometry (IMS), atmospheric pressure chemical ionization tandem MS (APCI MS/MS), or solvent extraction followed by GC/MS.

Although laborious and time-consuming, liquid–liquid extraction procedures have been used to study banknotes. In a study of Canadian currency, batches of banknotes were examined by dipping them in ethanol followed by liq-

uid–liquid extraction and analysis by GC/MS (*2*). Between 0.13 and 0.49 ng of cocaine was found on Canadian banknotes drawn from general circulation. Banknotes associated with criminal cases contained quantities of cocaine 50–1000 times higher. The overall recovery was reported as 35.6%, but the complexity of the method precluded detecting drugs other than cocaine, nicotine, and a few local anesthetics.

More recently, solid-phase extraction (SPE) using mixed-mode sorbents specifically designed for the isolation of controlled substances (*11*) have proved simple, sensitive, and specific for detecting controlled substances on banknotes (*3, 4*). Individual banknotes were extracted with methanol or dilute hydrochloric acid followed by addition of buffer, SPE, and GC/MS. Again, the only controlled substance detected was cocaine, with an absolute recovery >90%. SPE methods are applicable only to a limited range of compounds.

Supercritical fluid extraction (SFE), initially used to determine cocaine in human hair, has been applied to controlled substances (*12*). The reported ability to distinguish between trapped and chemically bound forms of cocaine (*13*) makes this a potentially useful technique for studying banknotes because it could reveal the time that has passed since a bill was in contact with the drug.

We have developed a technique for analyzing individual banknotes inserted for ~1 s between metal blocks heated to 285 °C (*14*). Ambient air, carrying the desorbed vapor, is drawn between the blocks into the plenum chamber of a modified tandem mass spectrometer. The advantages of this technique over the analysis of bundles of money include enhanced sensitivity and the ability to determine both the number of banknotes contaminated and the degree of contamination. The disadvantage is that it is a destructive process (to the analyte, not the banknote!) and cannot generally be repeated if requested by defense counsel. To some extent, this problem can be resolved by analyzing only a portion of each banknote.

Solvent extraction followed by GC/MS provides a high degree of confidence in the identification of any compounds present, although typically, only three ions characteristic of cocaine (*m/z* 303, 182, 82) are used. Quantification is also possible by using isotopically labeled internal standards (*6*). Another approach has been to use solvent extraction in combination with selective MS ionization. Positive ion CI GC/MS has been applied to the analysis of cocaine and its metabolites from biological specimens (*15*) and also to the detection of cocaine on a single banknote (*7*) by monitoring the protonated cocaine molecule (*m/z* 304).

Given that detectable amounts of controlled substances are found on notes in general circulation, unless a statistically significant number of banknotes is analyzed, the information gathered may still be inadequate to assess the likelihood of money being associated with drugs. The overall time required for solvent extraction makes such procedures unsuitable for analyzing large numbers of individual banknotes, though they are ideally suited for confirming results obtained using other techniques.

A recently developed technique called gold-labeled, optically read, rapid immunoassay (GLORIA), has been applied to the detection of controlled substances on banknotes (*16*). These "drug wipes" are supplied as disposable, single-test kits, available for opiates, cannabis, cocaine, and amphetamines. The wipes are based on an immunochemical detection process that uses antigen–gold conjugates. The test takes three minutes and is sensitive to nanogram quantities of analyte. The kits, together with controls, are usually retained as exhibits because the pink coloration, which indicates a positive finding, remains for many months after the test has been done. Drug wipes are typically used either as a preliminary screening method or as a secondary method to support results from other techniques.

Some concerns exist about the lack of specificity of immunoassay techniques. Although the test responds to the parent compounds and many or all of the metabolites, some false positives may occur due to fluorescent compounds from other drugs, food additives, or residues from medical investigation techniques. False negatives also may result from dilution, adulteration, filtration, or lack of appropriate detection limits (*17*).

IMS can reveal traces of controlled substances collected onto a filter paper, heated to vaporization, and ionized by electrons emitted by a ^{63}Ni source. The time required for the ions to drift through an electric field and impinge on a detector is measured, and the substances are identified by their "drift time" (Figure 2) (*18, 19*). Commercially available equipment is robust, portable, requires very little maintenance, and is widely used in airport and other security settings. It is a sophisticated screening method capable of detecting nanogram amounts of drugs and is ideally suited to operating in the field. IMS has been successfully used in drug counteroperations by the U.S. Drug Enforcement

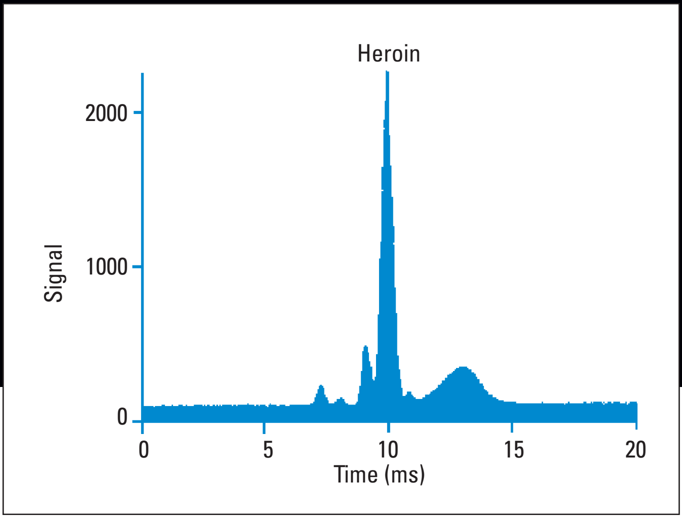


FIGURE 2. Heroin on banknotes by IMS.

Agency (*20*), the Canadian Revenue (*21*), and the U.K. Nottinghamshire Police (*22*).

IMS is a useful and economical screening technique, particularly when large sums of money are seized. Large quantities of banknotes are vacuumed of loose, surface-born particles. Subsequently, individual banknotes may be tested by collecting surface swabs, which are analyzed by insertion into the vaporizer unit of the IMS, or by directly inserting the banknotes themselves. Inserting the banknotes is approximately 1000 times more sensitive than vacuum collection. The combined evidence from this simple approach, together with confirmation by GC/MS or APCI MS/MS, has been presented in U.K. Crown Courts.

Direct thermal desorption of materials into the APCI source of a tandem mass spectrometer (*23*) allows rapid identification of microscopic quantities of target compounds from complex matrixes, such as household dust, without time-consuming sample preparation (*24*). Rather than collecting a full product ion spectrum, two or more characteristic precursor/product ion-pair transitions for each compound are monitored, yielding enhanced sensitivity without a loss in selectivity (*25*). Typically, samples are analyzed for the most common controlled substances, although the technique can be tailored to specific applications. Although no single analytical procedure can identify a compound completely unambiguously, this method provides a high degree of confidence.

The technique has been used to analyze particulates collected from bundles of U.K. banknotes (*10, 26*); both the frequency and amount of controlled drugs were compared with banknotes suspected of being associated with drug trafficking. Cocaine, heroin, and two heroin-related opiates were present above the detection threshold on banknotes from general circulation, but significantly larger amounts of these compounds were present on a greater proportion of the drug money. In addition, a significant number of confiscated banknote bundles were also contaminated with THC and 3,4-methylenedioxymethylamphetamine (MDMA, "Ecstasy").

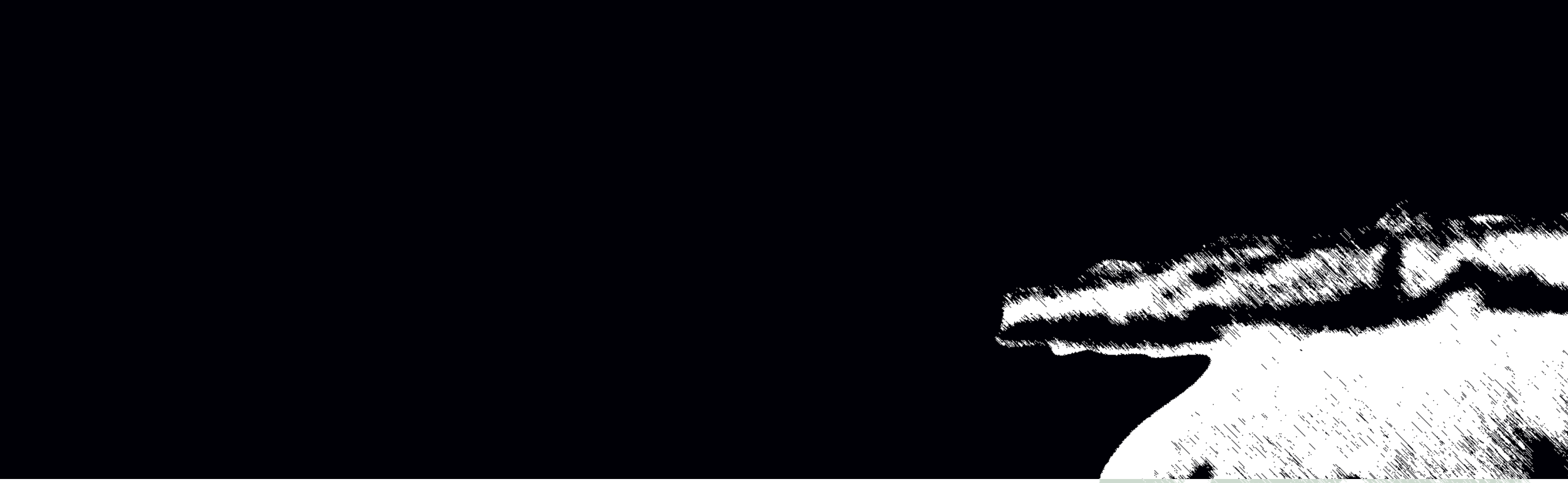
The individual banknote method (*14*) has now been used to sample a very large number of notes from a wide range of locations. It is abundantly clear that the majority of notes in circulation are contaminated with drugs, primarily cocaine. The advantage of this approach is that the results are presented to the analyst in real time, and thus appropriate decisions can be made about how best to proceed, such as the choice of sampling strategy or confirmatory analysis.

We analyzed 21 pieces of paper currency collected from various locations on a business trip from the United Kingdom to Canada and the United States (Figure 3). The notes were kept together in a well-used wallet. All but one showed a response to cocaine, the exception being a £20 banknote, and the largest response was from a $20 Canadian bill. The fifth note analyzed, a $1 USD bill, showed a response for diacetylmorphine, and the twelfth, a $20 USD bill, showed a small response to THC. No trace of MDMA was observed. We believe that this is the first report of heroin and THC contamination on U.S. currency from general circulation.

Precise quantification has not been attempted because of the difficulty of comparing responses from solutions with those from particulate materials trapped within the matrix of banknotes. It has been estimated that matrix effects attenuate the instrument response 15–20 fold. Although heroin contamination was noticeable on one note, the drug did not appear to have spread to any detectable extent to the other notes, despite their close proximity and similar handling over a period of several days. Similarly, while some of the notes exhibited relatively high cocaine contamination, notably the $20 Canadian bill, others showed minimal contamination.

What it all means

It is generally assumed that larger traces of controlled substances can be detected nearer to the initial contact with the drug, both spatially and temporally. In the case of paper money, drug particles within the matrix of a banknote will be abraded or augmented each time the banknote is handled, and equilibrium will be established. The upper limit of the general background quantity for cocaine on currency in the United States is 13 ng per banknote (*5*), whereas 13–100 ng amounts indicate closer contact with the original contamination. Although it is not possible to say how traces of drugs originated or how long they have been present, a



large quantity is consistent with direct contact.

The prevalence of cocaine may, at least in part, be attributed to the abuse of this compound through "snorting", the practice of inhaling drugs through the nose, which is sometimes effected with a rolled banknote. The relative ease with which cocaine can be isolated from banknotes is also reflected in the number of reports of its presence, in contrast with other drugs of abuse. Although amphetamine is also frequently administered in powder form, the crystal size is typically larger than that of cocaine, and retention by banknotes appears less effective. (Crystal sizes vary considerably, but sample studies reveal that the count geometric mean diameter for cocaine hydrochloride crystals is 1.4 µm, with a geometric standard deviation of 2.6 µm.) Cannabis usually occurs as either resin or dried leaves, which produce resinous surface deposits. Other drugs are usually administered in tablet form (e.g., MDMA), and material must be removed before it can be transferred to a banknote. LSD is considerably more potent than many other drugs, and, although the drug in its pure form is a crystalline solid, it is normally handled in solution and soaked into paper "tabs" for use. Because of the method of handling and usage, combined with the small doses used, it is unusual to encounter a detectable amount of the drug.

In an attempt to establish how recently banknotes had been in contact with controlled substances, bundles of banknotes were shaken inside polyester envelopes (*27*), assuming that recent contact would result in particles being loosely bound to the banknotes. The insides of the envelopes and some of the bundles were subsequently rinsed with methanol and the extract analyzed by GC/MS. The study concluded that cocaine was present on banknotes in general circulation, but detectable quantities were not removed by shaking.

Several commonly determined substances (e.g., diacetylmorphine and THC) are known to readily degrade in the presence of moisture and air. If these compounds are detected, recent contact with the drug can be inferred. When diacetylmorphine has degraded, it is sometimes possible to establish the presence of crude heroin by determining the more stable opiates narcotine and papaverine, which often persist in the mixture following acetylation of opium. Degradation products may also be sought, for example, benzoylecgonine in the case of cocaine.

Traces of controlled substances on banknotes could arise from contact with the drug itself, a contaminated hand, or another contaminated item. Thus, it is possible for an individual who has no personal involvement with drugs to be in possession of banknotes bearing detectable amounts of controlled substances. The mere presence of these compounds is, therefore, unlikely to be sufficient for a court to conclude that a quantity of money is linked with drugs. Several individual analyses should be conducted to assess both the quantities present and the frequency of contamination. In the event that money is linked to drug trafficking, one would expect to find that many, if not most, of the banknotes are contaminated. It is self-evident that the higher the frequency of contamination, the stronger the likelihood of direct involvement. From relatively few samples, it is not possible to claim that the contamination of a large quantity of money is widespread.

The study of cocaine contamination on Canadian currency stated that the most meaningful information would be gained by analyzing samples in batches according to denomination and comparing the amount per banknote from general circulation with seized money (*2*). Four batches of 100 banknotes of each denomination were analyzed; the extracts were combined, and an average amount of contamination was derived for each denomination in each batch. Using this method, it is impossible to comment on the origins of any drugs traces; the drugs found could come from a single banknote or could be equally distributed on all the notes. If individual banknotes are analyzed, it becomes possible to assess the extent to which contamination permeates a bundle.

As of August 1999, more than £100,000 worth of used Sterling currency from general circulation had been analyzed by the individual note technique (~5000 individual English, Scottish, and Northern Irish banknotes). The results broadly reflected results obtained from the analysis of banknote bundles (*8*); while cocaine contamination was widespread, the incidences of heroin, THC, MDMA, and amphetamine were rare, being found on <3% of banknotes. The total quantity of seized cash analyzed exceeded £8 million Sterling, comprising more than a quarter of a million individual notes. Although it has been demonstrated that cocaine can be transferred to and from banknotes by hand contact (*28*), it is also commonly asserted that a single highly contaminated banknote can contaminate a whole bundle; however,

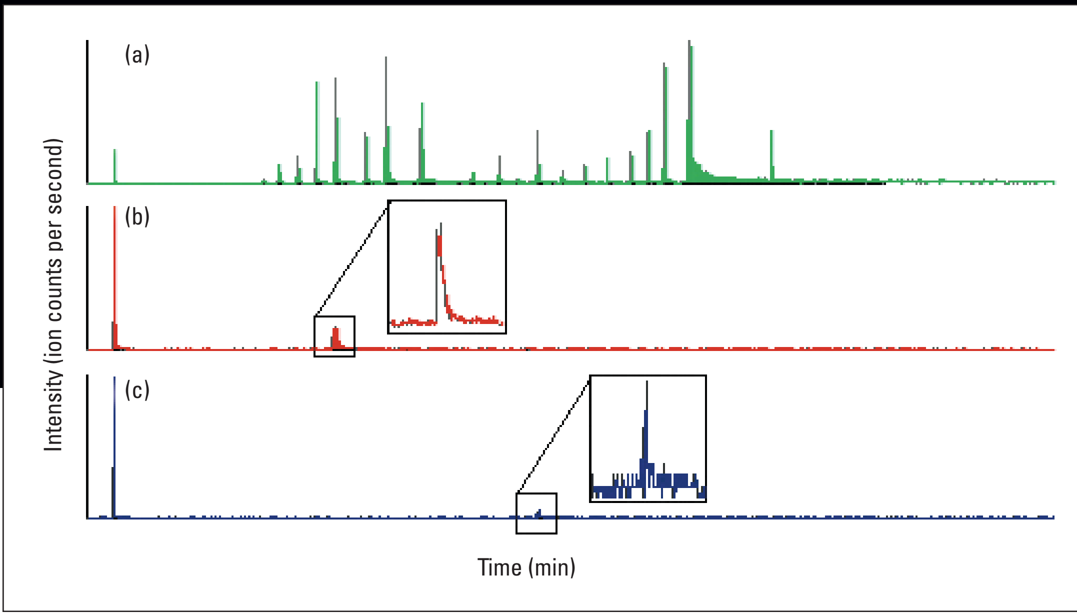


FIGURE 3. Tandem MS of banknotes (15 U.S., 4 Canadian, and 1 Sterling) of various denominations.

(a) Cocaine (*m/z* 304 → 105 transition), all 21 notes positive. (b) Heroin (*m/z* 370 → 268 transition), one $1 USD positive. (c) THC (*m/z* 315 → 259 transition), one $20 USD weakly positive.

very little evidence exists that this occurs.

For example, a Northern Irish banknote that produced a large instrument response for cocaine was placed between four other used banknotes that had shown no response for cocaine. The banknotes were then folded together and agitated to simulate normal handling. When the four outer banknotes were re-examined, <5% of the original quantity was observed to have passed to the two banknotes with which it had been in direct contact. The original banknote was still, by far, the most highly contaminated. Similar results have been observed for MDMA and other compounds, suggesting that at least some of the residues are bound to the fabric of the banknote and are not easily transferred through secondary contact. Transfer of material by means of primary contact is, therefore, a more likely cause of contamination than is transfer between banknotes, and traces are unlikely to significantly homogenize within or between bundles of cash during transport to the laboratory.

Counting machines may contribute to the wide dissemination of drugs on currency (*5*). Indeed, counting machines at the Bank of England have been shown to be contaminated with cocaine (*26*), probably resulting from the myriad banknotes counted daily. In one study, 50 sheets of paper banknotes with similar fiber characteristics to Sterling banknotes were cut to the size of £5 notes and dispatched to 60 different banks within England and Wales to be counted by routine methods (*29*). On return, the sheets of paper were analyzed by direct thermal desorption APCI MS/MS for various controlled substances. The sheets passed through the counting machine in reverse order to that in which they were analyzed, the first accumulating the most contamination, with less transferred to subsequent sheets. In contrast, the outer sheets of a manually counted sample showed significant contamination with cocaine. It is possible that these sheets were placed on a contaminated surface or were handled immediately after handling contaminated money. In total, 46% of the returned bundles of paper showed traces of cocaine. Overall, the levels of cocaine found on the sheets of paper were lower than those observed on the majority of banknotes from general circulation, which will have passed through counting machines many times. No drug other than cocaine was detected in a survey of more than 2000 analyzed samples.

The future

It is possible to differentiate "drug" money from "innocent" money. However, the interpretation of the significance generally relies on the experience of the analyst. Such factors as the proportion of banknotes contaminated with a particular compound and the extent of contamination need to be considered and compared with money taken from general circulation. Simplistic yardsticks, such as defining a contamination threshold for individual notes, only tell part of the story because they fail to monitor absolute concentrations. Reporting the percentage of contaminated banknotes disregards the extent of contamination on individual notes, and the percentage will, of course, vary according to the detection limit of the particular analytical approach used. A unified approach is needed whereby results obtained using different techniques and at different laboratories can be meaningfully compared. Because a statistically significant number of analyses are required, it seems likely that one of the rapid approaches, such as thermal desorption followed by IMS or APCI MS/MS, will become the standard against which other techniques are compared.

Further work is now in progress to demonstrate how drug traces can be correlated with bulk quantities of material. It is sometimes possible to characterize controlled substances by profiling other compounds present (e.g., natural products, cutting agents, and contaminants). Because differ-

ent materials adhere to banknotes with varying degrees of tenacity, and sample collection and analysis may further discriminate between different components, the profile of a drug trace rarely reflects the constituency of the bulk sample. We anticipate that characterizing the stable isotopic composition of the active components will permit such matches.

The authors wish to thank John Moss for work on trapping mechanisms and Joanna Parry for the counting machines work. Bill Davidson and Bill Stott of Sciex assisted in the design of the thermal desorption unit manufactured by John Luke.

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(28) ElSohly, M. A. *J. Anal. Toxicol.* **1991,** *15,* 46.

(29) Parry, J. Investigation of Sources and the Ability to Trace Cocaine Residues. BSc. Thesis, University of Bristol, U.K., 1998.

Richard Sleeman is scientific director and Fletcher Burton is the forensic manager of Mass Spec Analytical Ltd. (United Kingdom). Their main research interest is developing rapid sample introduction techniques for real-time trace analytical applications. Jim Carter is research associate in MS at the NERC Organic Mass Spectrometry Facility and is interested in developing applications for organic and stable isotopic MS. Dave Roberts is a lecturer with research interests in method development for trace substances in environmental samples. Both are based at the University of Bristol (United Kingdom). P. Hulmston is scientific support manager and head of the scenes of crime department of the Nottinghamshire Police. He is particularly interested in the application of trace drug detection and identification technology to support police counter drug operations. Address correspondence to Carter at School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 ITS, United Kingdom (jim.carter@bristol.ac.uk).

Attachment C18

Jourdan, T.H., Veitenheimer, A., and Wagner, J.R., Exploration Of Cocaine Contamination of United States Currency – Continuing Studies, *Proceedings Am. Acad. Forens. Sci.*, (2010).

A86 Microcrystal Analysis of Cocaine Hydrochloride and Added Adulterants

Hannah C. Nelson, BS, University of Alabama at Birmingham, 1201 University Boulevard, Birmingham, AL 35294; Elizabeth A. Gardner, PhD, University of Alabama at Birmingham, Department of Justice, UBOB 210, 1530 3rd Avenue, South, Birmingham, AL 35294 4562; and Dan Matteo, MSFS, Alabama Department of Forensic Sciences, 2026 Valleydale Road, Hoover, AL 35244*

After attending this presentation, attendees will have a basic understanding of microcrystal tests, the effect of adulterants on cocaine microcrystal morphology, and general trends to observe when performing microcrystal tests on cocaine.

This presentation will impact the forensic science community by shedding new light on an old technique by showing trends in crystal behavior of cocaine when diluted with common adulterants. It will demonstrate that microcrystal tests are specific enough to be used in drug analysis. The techniques developed in this project have potential application in drug profiling to track both local and international trafficking patterns.

Microcrystal analysis of drugs, once used as a confirmatory test, has gradually been replaced with more sophisticated technology; however, these tests still have a place in forensic labs. The objective of this project was to investigate the changes in the crystal morphology of cocaine in the presence of the common adulterants, caffeine and lidocaine.

The observed changes in the morphology of the cocaine crystals were unique to both the specific adulterant and the concentration of that adulterant. Similar trends were seen for aqueous and powder samples. Cocaine/caffeine mixtures can be identified by the appearance of curved short axes. The degree of curvature increases with caffeine concentration, until at fifty percent caffeine, sphere shaped branched crystals appear. The crystal formation was also delayed in the presence of caffeine.

Unlike caffeine, the changes in crystal morphology of cocaine in the presence of lidocaine were seen immediately. Lidocaine adulterant can be identified by longer, thinner crystals with an X shaped short axis. As the lidocaine concentration increases, the crystals become x shaped and at fifty percent lidocaine, the crystal form an X with the presence of few non branched spherical crystals.

The results show that the cocaine crystal morphology does change in the presence of an adulterant. Distinct trends were observed with each adulterant at each concentration.

Current work on this project includes examining the crystal habit of cocaine mixtures of procaine, benzocaine, table sugar, baking soda, and levamisole.

Microcrystal, Cocaine, Adulterants

A87 Exploration of Cocaine Contamination of United States Currency – Continuing Studies

Thomas H. Jourdan, PhD, Forensic Science Institute, University of Central Oklahoma, 100 North University Drive, Box 203, Edmond, OK 73034; Allison Veitenheimer, BS, 801 Northern Trace, Keller, TX 76248; and Jarrad R. Wagner, PhD, Department of Forensic Sciences, Oklahoma State University CHS, 1111 West 17th Street, Tulsa, OK 74107*

The goals of this presentation are to continue the development of the understanding of the contamination of U.S. currency resulting from illicit cocaine trafficking, as well as to introduce a survey of several foreign currencies for similar contamination; and to offer a mathematical model which seeks to assign a numerical probability of drawing from currency in general circulation bills contaminated at the levels quantitated in evidence submissions to the FBI Laboratory associated with forty criminal investigations involving drug trafficking and money laundering.

This presentation will impact the forensic science community by providing information on an analytical protocol developed for quantitation of loosely bound cocaine residue levels on currency, and a mathematical model offered regarding the interpretation of the resulting values for U.S currency.

This study, early results of which have been reported to the Academy (1997 and 2003), had its beginnings in response to a 1994 decision by the 9th Circuit Court of Appeals in the case of U.S. v. U.S. Currency (Alexander), 39 F.3d 1039, in which the court(s) acknowledged the wide spread contamination of the U.S. currency supply by the illicit cocaine importation trade. The argument has been put forth and a former FBI Laboratory forensic examiner, successfully so during expert witness testimony in federal court on several occasions, that the absolute amount of the drug on currency, and not its mere presence, is probative.

The ink on U.S. currency never really dries. In effect, one can conceptualize currency as in a microscopic sense a "sticky" surface on to which, as it is circulated, various oils (e.g., human sebaceous) and miscellaneous environmental dirt and grime (including residue amounts of drugs of abuse) become attached. In the case of cocaine, a person who has handled the drug the then handles currency transfers residue in the low hundreds of nanograms range to the bill(s), and that this amount over the course of subsequent circulation and manipulation is reduced to a steady state "background" level.

A study has recently been completed of the currency in general circulation in the U.S. Quantifiable levels of cocaine have been encountered on more than ninety percent of the bills thus far examined. Because it is unlikely that members of the illicit drug trade have actually physically handled this volume of bills, it was presented during a 1997 presentation to the Academy that some other agent is responsible for the extent of the distribution of the drug on currency in general circulation, in particular submitting that this agent is the mechanical currency counters which are universally employed in financial institutions have had a "homogenizing" effect on the currency supply.

The sampling aliquot for this study is $1,860, which translates to ten bills of each common U.S. currency denomination ($1, … $5, … , $100). Thus results are reported by location and by denomination. The initial screening is performed with a Barringer Instruments IONSCAN ion mobility spectrometer (IMS), an instrument with nanogram sensitivity for a number of the commonly encountered drugs of abuse, and cocaine in particular. Confirmation and quantitation is accomplished using liquid chromatography mass spectrometry mass spectrometry (LC/MS/MS) on

an Applied Biosystems API4000Q instrument with Shimadzu LC. A deuterated internal standard is introduced in the extraction solvent in the initial step of the quantitation process so as to eliminate potential errors associated with subsequent manipulations. Currency aliquots from some 70 locations in 42 states have been surveyed (quantitated). In addition, currency from on the order of ten foreign countries has been similarly surveyed.

Following plotting of the background currency data (frequency as a function of contamination level in ng/bill) the equation of the resulting curve has been established and the function then normalized. Integration from zero to a particular contamination level, i.e., one from a given criminal case, with subsequent subtraction from 1.00, estimates the probability of drawing a bill from general circulation contaminated to that particular extent or higher.

Cocaine Residue Recovery, Quantitation of Cocaine on Currency, Interpretation of Cocaine Currency Contamination

A88 The Scientific Working Group for the Analysis of Seized Drugs (SWGDRUG)

Scott R. Oulton, BS, Southwest Laboratory, 2815 Scott Street, Vista, CA 92081*

After attending this presentation, attendees will discuss the current status of SWGDRUG's work products. Representatives from the SWGDRUG Core Committee will answer questions and address the concerns of the attendees.

This presentation will impact the forensic science community by providing the current work products by SWGDRUG as it relates to the analysis of seized drugs.

The objective of this presentation is to update forensic drug analysts on recent work products from the Scientific Working Group for the Analysis of Seized Drugs (SWGDRUG). Currently, SWGDRUG is working on the following topics:

- Examples for the estimation of uncertainty of measurement in weight determinations;
- Revising/updating current SWGDRUG Recommendations;
- Developing standard training competencies.

These topics have been widely discussed in the forensic science community. During this presentation, the current status of SWGDRUG's work products will be discussed. Representatives from the SWGDRUG Core Committee will answer questions and address the concerns of attendees.

In past presentations to the American Academy of Forensic Sciences, a synopsis of the history of SWGDRUG and goals of the core committee have been presented. This year's presentation will focus on the specifics described above. However, the following information is presented here for those unfamiliar with the SWGDRUG process. SWGDRUG has been in existence since 1997. The mission of SWGDRUG is to recommend minimum standards for the forensic examination of seized drugs and to seek their international acceptance.

The objectives of SWGDRUG are the following:

- Specifying requirements for forensic drug practitioners' knowledge, skill and abilities;
- Promoting professional development;
- Providing a means of information exchange within the forensic science community;
- Promoting ethical standards of practitioners;
- Providing minimum standards for drug examinations and reporting;
- Establishing quality assurance requirements;
- Considering relevant international standards; and,
- Seeking international acceptance of SWGDRUG recommendations.

The SWGDRUG core committee is comprised of representatives from federal, state and local law enforcement agencies in the United States, Canada, Great Britain, Germany, Japan, Australia, the European Network of Forensic Science Institutes (ENFSI), the United Nations Drug Control Program (UNDCP), forensic science educators, the American Society of Crime Laboratory Directors (ASCLD), ASTM, and the National Institute of Standards and Technology (NIST). Published recommendations are available on the SWGDRUG website located at: www.swgdrug.org.

Analysis of Drugs, SWGDRUG, Seized Drugs

A89 PCR Optimization of a Highly Polymorphic Marijuana STR Locus on Collection Cards for High-Throughput Screening

Heather M. Coyle, PhD, University of New Haven, Forensic Science Department, 300 Boston Post Road, West Haven, CT 06516*

After attending this presentation, attendees will have a better understanding of evidence archival for plant DNA and how plant DNA can be useful as forensic evidence.

This presentation will impact the forensic science community being that this is the first time collection cards and automation for plant data basing has been presented in a useful forensic context that could be implemented in all forensic laboratories and for crime scene personnel for marijuana typing.

The genetics of marijuana has long been undefined and a better understanding of the different relationships of *Cannabis* cultivars would be useful in trying to understand different grow operations and for tracing drug distribution patterns. As such, a DNA based bioinformatics classification program using a variety of genetic markers and methodologies is being initiated. A series of different markers have been identified and published in the scientific literature in recent years; however, evaluating which markers would be ultimately the best to use (based on power of sample discrimination) is challenging at the population level. A polymorphic hexanucleotide repeat STR locus (NMI01) was selected as a genetic marker to screen our samples for initial classification by DNA. As our samples are sorted into groups, we will add more markers to determine if further individualization of the samples can be accomplished as deemed necessary from the data.

As an initial step, one goal was to define a convenient, long term archival system for plant DNA typing of marijuana (*Cannabis sativa* L.). Forensic evidence collection and archival of plant evidence is typically performed by collecting leaf samples in coin envelopes and air drying the sample for later trace evidence analysis. Collection cards, however, are utilized for human DNA database archival of blood and saliva fluids and are considered valuable for long term preservation of DNA evidence and for high through put processing by PCR. Samples on these cards are stable for several years at room temperature storage. These cards are also pre treated with chemicals that lyse cells, denature proteins and protect nucleic acids from nucleases, oxidation and ultra violet irradiation damage as well as preventing mold and bacterial growth.

EXHIBIT 6

IN THE
UNITED STATES DISTRICT COURT
OF THE NORTHERN DISTRICT OF ILLINOIS
EASTERN DIVISION

UNITED STATES OF AMERICA Plaintiff, vs. FUNDS IN THE AMOUNT OF ONE, HUNDRED THOUSAND AND ONE HUNDRED TWENTY DOLLARS ($100,120.00 U.S.C.), Defendant. NICHOLAS P. MARROCCO, and VINCENT J. FALLON, Claimants.	)	No. 03 C 3644 The Honorable Elaine E. Bucklo, District Judge, Presiding CATHERINE A. WILLIAMS NOTARY PUBLIC STATE OF IDAHO

State of Idaho)
) SS.
County of Twin Falls)

Affidavit of Dr. Lawrence J. Myers

I, Lawrence J. Myers, DVM. MS. PhD, first being deposed and sworn, state the following:

1. That your affiant is of legal age, sound mind, and under no legal disability.
2. The opinions stated or expressed are based upon my training, education, experience, and research described by my *curriculum vitae* attached as Exhibit A. If called to testify, I would testify the statements made in my C.V. are true and correct.

3. That your affiant has a Master of Science in Zoology/Ethology; Ethology is the scientific study of animal behavior. Additionally, your affiant has a doctorate in neurophysiology and doctorate in veterinary medicine.

4. Your Affiant's academic career in the Department of Physiology and Pharmacology, College of Veterinary Medicine, at Auburn University beginning in 1982 and continuing through the present, is more fully detailed in my attached C.V.

5. During your Affiant's career, he has had an opportunity to author and co-author numerous scientific research articles. A partial list of this scientific work is described in your Affiant's C.V. in subsection 5.C. All the articles listed in the C.V. are peer-reviewed articles.

6. My opinions are based on my own original research, which I have been conducting since 1982, continuing to the present day, and upon reading the research of others, which is related to that research. My *curriculum vitae* provides details as to my work and research. In particular, I founded the Institute for Biological Detection Systems at Auburn University in 1989 for three purposes: (1) to research the practical application of the use of dog-handler teams to detect a variety of targets of interest, (2) to research basic physiology of organisms to better understand how to optimize the use of the detector dog and (3) development of artificial biosensors. At the time of its founding, it was the largest research operation in the United States devoted to such research. The Institute was funded by the Technical Support Working Group ("TSWG"), a federal interagency funding mechanism for a

variety of federal agencies. Attached as Exhibits B and C are print-outs of the "home" and "about" pages from the TSWG website, found at http://www.tswg.gov/.

7. All of my opinions recited herein are to a reasonable degree of scientific certainty based upon my aforementioned training, education, experience, and research.

8. I have been declared to be an expert in sensory function and behavior of the dog, in behavioral experimental design, and in the use of detector dog-handler teams in federal and state courts. I have been permitted to offer my opinions to a reasonable degree of scientific certainty in cases where I have been called on behalf of the United States, of various law enforcement agencies and of private defendants.

9. Your Affiant does not have a precise number of cases where I have testified as an expert. However, the following is a partial list of cases in which the court allowed me to testify as an expert:

   a. *State of California vs. Tobias White*, March 12, 2007
   b. *State of Louisiana vs. Jan Waters*, March 2, 2006
   c. *United States vs. Torrey L.*, September 13, 2007
   d. *State of California vs. Ronald Thomas*, February 25, 2005
   e. *United States vs. Sugar, et. al.*, October 27, 2003
   f. *People vs. Juan Manuel Ruiz*, September 15, 2003
   g. *United States vs. Eric Robert*, January 26, 2004
   h. *United States vs. David Negron*, September 16, 2005

i. *People vs. Mitchell*, July 18, 2003

j. *United States vs. Jose Luis Aviles-Luna*, March 18, 2004

k. *People v. Bailey Jackson, Jr.*, August 30, 2004

l. *United States vs. Michael Brent Gomillion*, February 4, 2004

m. *State of California vs. Lewis Gray*, August 8, 2005

n. *State of California vs. Izell B. Gaston*, December 16, 2004

o. *People vs. Flores*, February 4, 2004

p. *United States vs. Manuel Diaz*, March 15, 2006

q. *United States vs. Torrey Glenn and David Crenshaw*, October 24, 2007

r. *People vs. Melvin Corbin*, January 5, 2005

s. *County of Los Angeles vs. Antonio Barba*, May 16, 2005

t. *County of Los Angeles vs. Marvin Corbin*, January 5, 2005

u. *County of Los Angeles vs. Michael Harris*, August 9, 2002

v. *County of Los Angeles vs. Stephon White*, Jr., February 26, 2002

w. *County of Los Angeles vs. Calvin Johnson*, October 21, 2003.

10. I have examined documents, records, and testimony provided to me by Stephen Komie and Brian King relating to the case of *United States v. $100,120.00 in U.S.C.*, 03-cv-03644. These include, but are not limited to, the sworn affidavit of Sanford A. Angelos, the affidavit of David Kroyer, the transcript of a motion to suppress, which included the testimony of Eric Romano, Sterling Terry, and Richard King, training records for Richard King

and the dog, Deny, the Chicago Police Department Training Division "Certificate of Achievement" for Richard King and the dog, "Deny," the affidavits of Richard King dated 6/24/10 and 12/21/10, and a report drafted by Stefan Rose. Additionally, subsequent to my preliminary opinions, I have been told that the Plaintiff filed a third motion for summary judgment. I was provided with and reviewed a memorandum of law in support of the motion for summary judgment and a statement of material facts with exhibits, both filed on or about May 27, 2011. Finally, I have also examined pertinent peer-reviewed literature, some of which is cited at the end of my report.

11. It is my opinion to a reasonable degree of scientific certainty that a positive alert by the dog Deny in the company and control of his handler, Richard King, does not support the theory that the currency was recently, or just prior to packaging in close or actual proximity to a significant amount of narcotics.

12. Whether Deny can reliably detect actual narcotics is the first question. The other question, which is one central to this case, is whether or not Deny is reliable in locating drug-tainted currency.

13. There is no scientific evidence to support the theory that Deny's reliability in the field as to drug seizures translates to reliable identification of drug-tainted currency. The two situations, finding of drugs and the determination of narcotics contamination on currency, are not one and the same. The first can be borne out, partially, by the actual

seizure of identified drugs; the other does not have proof as there are no actual narcotics seized.

14. There is no scientific evidence that the reliability of the dog-handler team of King and Deny has ever been determined. There are no records of replicated, controlled, randomized, double-blind tests performed to determine reliability. The team's reliability is only attested to by the opinion of the handler and an annual certificate issued by the Chicago Police Department Training Division without a description of how such certificates are earned. Moreover, there is no testimony of any specialized expertise on the part of the handler, Officer King, to competently render such an opinion regarding the reliability of the canine.

15. There are no records or testimony that the dog-handler team engaged in double-blind training. One of the hallmarks of the scientific method is replication through experimentation of proper design. A single blind test is one in which the test subject or participant is unaware of the conditions which could skew the result due to participant bias. A double-blind test is one in which such conditions are withheld from both the participant and the researcher or observer. In experimental testing conditions for a canine detection team, the canine handler (Officer King) represents the participant, and the trainer usually represents the observer or researcher.

16. The lack of such blind training has been shown to result in teams that utilize cues by the handler to alert rather than actually utilizing the odor

of the desired target. (Gordon, *et al.*, 2008; Lit, *et al.*, 2011). Thus, the importance of the blind testing is to insure that the canine's alert is based on utilization of the specific target odor and hence that the canine's alert is a reliable indicator of the presence of the target odor.

17. Second, your Affiant is aware that it has been demonstrated many times in various scientific research articles and studies that general circulation currency is contaminated with narcotics. These scientific studies have concentrated upon cocaine HCl. However, your Affiant is aware of at least one study which did find that general circulation currency is contaminated with other narcotics, such as amphetamine, methamphetamine, heroin, and PCP. (Jenkins, A.J., *et al.,* 2001)

18. There is no evidence of numerous non-alerts by the canine, Deny, to circulated U.S. currency. There is no evidence in the records provided that the dog Deny was trained to reliably discriminate narcotics contaminated currency from general circulation currency. In fact, there are only three instances of the dog being trained on contaminated currency, and no evidence of training being performed to ensure discrimination by the dog between contaminated and general circulation currency. So, once again, there is no real basis to believe that Deny is reliable in alerting upon drug-contaminated currency in the real world.

19. Discrimination between general circulation currency and drug-contaminated currency is important since there are numerous scientific studies showing that general circulation currency in the United States is

contaminated with trace amounts of illegal drugs. Further, it is also known, the currency itself has an odor detectable by the dog. U.S. Customs in the 1990's trained dogs to detect large quantities of U.S. currency. There are also certainly other contaminating odors on U.S. currency. Hence, it must be insured that a trained drug-detection dog be trained to alert to the drugs of interest alone, rather than having inadvertently been trained to alert to very low, normal levels of drugs on currency or the odors of currency such as inks or extraneous odors found on currency.

20. Third, your Affiant is of the opinion to a reasonable degree of scientific certainty that "proofing" a dog off general circulation currency is absolutely necessary in order to insure reliability of the canine in the field. Proofing is a term of art to dog trainers, which in this context means training a dog to discriminate between general circulation currency and currency which has recently, and intentionally, been contaminated with significant amounts of the odor of narcotics. Because it has been demonstrated that general circulation currency has been contaminated with trace amounts of narcotics, it is necessary to proof dogs off of general circulation currency.

21. Your Affiant is of the opinion to a reasonable degree of scientific certainty that an additional problem exists, which requires the proofing of a canine narcotics detection dog off the odor of United States currency. When a canine is trained to detect the odor of narcotics and these narcotics odor

is then used to contaminate currency, even uncirculated currency, the canine will associate the odor of the general circulation currency with its previously trained target, the narcotics odor. Since this new odor (currency) is reinforced by the handler/trainer, the new associated odor is added to the repertoire of targets the dog attempts to locate and alert upon.

22. To illustrate this in a hypothetical, assume that one is attempting to train a canine to detect the odor of a certain narcotic. Also, assume during training, a minute sample of the narcotic was always presented to the canine in a plastic, Zip-loc baggie. After a certain amount of training, the canine may successfully learn to detect the odor of the narcotic contained in the Zip-loc baggie. However, the problem is that the canine will not be able to differentiate or discriminate between the narcotic odor and the odor of the Zip-loc baggie as desired targets. To the canine, it is unaware what precise target odor it is being rewarded for alerting upon. Therefore, the canine does not discriminate between the plastic odor of the baggie and its narcotic contents; it will likely alert to the presence of the odor of the baggie, the narcotic, or a combination of the two.

23. In order to prevent a false alert to empty Zip-loc baggies, one must proof the dog off the odor of the baggie, itself. Turning back to the real world, the currency (and its signature odor) is analogous to the Zip-loc baggie. Without adequate discrimination training, the odor of the currency (i.e.,

the linen, ink, etc.) simply becomes another target odor upon which an alert by the canine yields a reward.

24. Fourth, there are a wide variety of behaviors on the part of a human that cue behaviors in dogs, including pointing, gazing at a particular area, and other gestures (Miklosi, *et al.*) It is important to understand that these human behaviors may be completely unintentional on the part of the human subject.

25. Suspicion by the handler that an item is the target of the search has been shown to cause dogs to frequently false alert on items. (Lit, *et al.*, 2011) The Lit study illustrates that the potential for cuing is not remote, but rather highly probable. In the study, narcotics and explosive detection dog teams were deployed under testing conditions in which no target odor was present. However, the handler teams were led to believe that there were in fact target odors present. Thus, any alert exhibited by the dogs were false alerts because there were no narcotics or explosives present in the testing environment. The results were that in 144 separate runs, there were a total of 225 alerts issued, because there was the possibility of multiple alerts within each run. It is worth re-stating that because there were no narcotic or explosive odors present, all 225 alerts were false alerts. Out of the 144 runs, only 15 percent were completed without any alerts. Thus, in 85 percent of the runs, at least one or more false alerts were exhibited by the dogs.

26. The Lit study is just one study, which shows the very real problem with unintentional cuing. However, this phenomenon, sometimes referred to as the "Clever Hans effect," has been known for well over a century. In the early twentieth century, a horse by the name of Clever Hans was believed to be capable of counting and other simple mental tasks. A psychologist researching the incredible horse discovered the horse was, in fact, recognizing and responding to minute, unintentional, postural and facial cues of his trainer or individuals in the crowd. In other words, animals have the ability to recognize and respond to subtle cues provided by people around them. And canines are especially adept with this ability as it relates to humans.

27. Relating the concept of cuing to this case reveals, the description of the sniff search suggests that the handler knew and saw the object of the search prior to the search. (Report of Proceedings, April 26, 2004 at pp. 14, 86, 198.) The description of the search points out that the officer placing the briefcase was visible in the doorway of the room in which it had been placed during the search by King and Deny. (*Id.* at p.199) This allowed the officer to influence the behavior, however unintentionally, of the handler King as well as the dog, Deny.

28. The description of the search by the dog handler strongly suggests that the briefcase was in plain sight and there is no evidence that any similar items were in the room in which the "test" was performed. (*Id.* at 15-16.) This being the case, and in conjunction with the knowledge of the

handler as to what the target was and the presence of the officer placing the briefcase, the handler King would have known or strongly suspected that the briefcase was the item of interest.

29. Under these conditions, the danger of cuing the dog, either intentionally or unintentionally, renders the results of the search meaningless and completely unreliable.

30. Your Affiant is of the opinion to a reasonable degree of scientific certainty that the canine handler's averment that "[Deny] never passed by anyone and suddenly made a turn for their wallet or purse," carries no weight whatsoever, because drug dogs are trained to search for drugs on command only. This statement, by the handler, demonstrates a complete lack of scientific understanding as to canine training and behavior.

31. Your affiant fully agrees with Plaintiff's statement that subjective belief or unsupported speculation should be excluded. Your affiant is of the opinion that this is precisely why Deny's purported alert should be excluded from this case.

32. Therefore, it is my opinion to a reasonable degree of scientific certainty that a positive alert by the dog Deny in the company and control of his handler, Richard King, does not reliably support the theory that the currency was recently, or just prior to packaging in close or actual proximity to a significant amount of narcotics.

33. Further affiant sayeth naught.

Dr. Lawrence J. Myers

CATHERINE A. WILLIAMS
NOTARY
PUBLIC
STATE OF IDAHO

Subscribed and Sworn to before
me this 30 day of August, 2011.

Notary Public 3-3-12

Literaure Cited:

Robert T. Gordon, Carole Beck Schatz, Lawrence J. Myers, Michael Kosty, Constance Gonczy, Joan Kroener, Michael Tran, Pamela Kurtzhals, Susan Heath, James A. Koziol, Nan Arthur, Madeline Gabriel, Judy Hemping, Gordon Hemping, Sally Nesbitt, Lydia Tucker-Clark, Jennifer Zaayer. The use of canines in the detection of human cancers. *The Journal of Alternative and Complementary Medicine.* 14(1): 61-67, 2008.

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EXHIBIT 7

IN THE UNITED STATES DISTRICT COURT
NORTHERN DISTRICT OF ILLINOIS
EASTERN DIVISION

UNITED STATES OF AMERICA Plaintiff,	) Cause No.: 03-cv-03644
v.	)
FUNDS IN THE AMOUNT OF $100,120 Defendant.	)

NICHOLAS P. MARROCO, and
VINCENT J. FALLON,
Claimants.

AFFIDAVIT

COMES NOW, David Kroyer, and under oath and subject to the pains and penalties of perjury, hereby swears to the following:

1) Credentials:

Owner, President, Certified Training and Behavior Consultant, Master Trainer and Training Director of Canine Headquarters Police K9 division. Eleven years training experience. Placed green and finished K9 detection dogs for Law Enforcement, Military, and Homeland Security/Border Patrol. Trained and placed handlers for Law Enforcement, and Military. One Hundred percent (100%) passing rate under NNDDA certification. Conducted seminars and workshops nationally and internationally on detection dog training. Assisted in developing a program for mine detection rats at Bogota University ,Columbia.

2) My statements and opinions in this affidavit are based on my knowledge and experience in the field of Canine Specific Odor Recognition. However, I also have experience in the following canine fields:

a. Patrol and Criminal Apprehension
b. Behavior Modification
c. Obedience
d. Sport Work (International Police Organization ,French Ring, Mondio Ring, Agility, Protection Sports Association)
e. Sport Tracking and Man Trailing

3) If permitted to testify in this case, statements and opinions in this affidavit are offered with a reasonable certainty in the field of Canine Specific Odor Recognition.

4) I have reviewed transcripts from a Motion To Suppress, Government Memorandums, Government Statement of Facts, Officer King's affidavit, the K9 training logs, field logs, certification, the Courts' Memorandum opinion concerning the Motion to Suppress, and various scientific studies and documents connected with this case.

5) K9 "Deny" was certified by the Chicago Police Department, the agency which trained Deny. It does not specify on his certification which odors the dog is certified to detect. It is normal in the industry to not only have an inter-departmental certification which specifies which odors the dog is trained to detect, but also a certification by an outside agency, such as NNDDA (National Narcotic Detector Dog

Association), or NAPWDA, or any of the other recognized organizations. This will show that an unbiased outside source has certified the K9. Neither the certification nor the handler's affidavit specify the qualifications or credentials of the Assistant Deputy Superintendent who certified the K9. Neither the certification nor the handlers affidavit specify the standards K9 Deny needed to achieve to become certified.

6) The K9 in question was apparently trained to alert or indicate on tainted United States Currency (hereinafter "USC"). It is an industry standard to proof the dog or also use untainted/uncirculated USC in training to assure the dog is not indicating or learning to indicate on untainted USC. In the training log of K9 Deny, there is only one entry of a training scenario where untainted USC was used. I believe it was on July 16 1998 at 1300 hours. A training scenario was set up in a classroom where it states "Numerous Unscented Money" was used in training. It also states that cocaine scented money was used. It then states that the K9 had a "positive alert" indicated by "pos" on the training log. In my opinion, this shows that Deny alerted positively on untainted money. I believe it is inconclusive to determine whether K9 Deny can differentiate between untainted and tainted USC.

7) In the testimony of the police officer, its states that the room K9 Deny searched and indicated POS on the briefcase of USC, was indeed used before for the same purpose and was not a clean or uncontaminated room. It is very important that steps are taken to have a "clean" room, as a dog can be very proficient at detecting residual odors of narcotics, immeasurable by modern technology. A residual odor is an odor left behind of an immeasurable weight. Example: If 5 grams of a narcotic was set as a training aid in a filing cabinet, and then removed after training, it is possible for a dog to detect the residual odor many days after the narcotic was removed. Based on my experience and opinion, in order to ensure the reliability of the K9's alert/indication in specific odor detection, the handler should have taken the following measures:

   a. Make sure narcotics have not been in the room in the recent past.
   b. Perform a controlled search of the room with a "control" sample of verified, untainted USC secreted in the room.
   c. Perform a 2nd search of the room, this time with both the verified untainted USC and the sample in question secreted in the room.

8) In this case, the Government appears to be relying on a study of trace narcotics on USC. In the Furton study, only Methyl Benzoate was used as a scent for the K9. There is no evidence in the handler's affidavit or training logs that K9 Deny was trained with pseudo cocaine. In fact, it appears that K9 Deny was trained with 93% illicit cocaine. In my expert opinion, I cannot agree with the governments' theory that K9 Deny alerted because the only odor available on the currency was that of methyl benzoate.

9) In the study by Furton, he used pure methyl benzoate; he did not use street cocaine. Illicit cocaine is not pure and has cutting agents such as baking soda, B12 and other agents that a dog will put in its repertoire of odors he gets rewarded for indicating on. In the logs of K9 Deny, it states that he has numerous positive alerts on street or tainted currency which he was rewarded for. I do not see information if K9 Deny has been proofed on untainted currency or cutting agents. These findings make it inconclusive as to whether K9 Deny can truly detect tainted currency vs. untainted currency.

10) Finally, based on my experience and knowledge of a K9's ability to detect residual odors and the general widespread contamination of U.S.C., I am of the opinion to a reasonable degree of certainty in the field of canine specific odor recognition that a positive alert by Deny to the currency in this case could have been caused because:

   a. the room in which the search took place was contaminated;
   b. Deny was not properly trained to discriminate between tainted currency and uncirculated, untainted currency;

c. the currency was innocently owned, contaminated currency in general circulation; or
d. of any of the aforesaid reasons provided in this affidavit.

Further Affiant Saith not.

David Kroyer

NICHOL LYNN HORTON
Notary Public, State of Texas
My Commission Expires
July 27, 2013

Nichol Lynn Horton

EXHIBIT 8

Courts Reject Drug-Tainted Evidence

Studies find cocaine-soiled cash so prevalent that even Janet Reno had some

The only evidence South Florida police had against Leroy Lord was the drug-tainted, rolled-up dollar bill they saw him drop. But it was enough to persuade a jury to find him guilty of possessing cocaine.

Police say traces of cocaine on the money proved Lord had placed the drug on or near the bill. But in April, the Florida Third District Court of Appeals followed a growing trend in reversing the conviction.

"Cocaine in South Florida is so pervasive that microscopic traces of the drug can be found on much of the currency circulating in the area," the appeals court said in *Lord v. Florida*, No. 91-2147. "The mere presence of trace amounts of cocaine on a common object ... is insufficient to support a felony conviction for possession of cocaine."

Lawyers say the Florida ruling is the latest in a series of decisions in which judges have reversed convictions and returned seized property because the only evidence is trace amounts of drugs. These cases are citing evidence that the scent of cocaine is found on most currency and often will trigger the sensitive noses of dogs trained to detect drugs.

A forensic chemist who is asked to testify in more than a dozen cases annually, Dr. James Woodford of Atlanta is convinced that cocaine contamination is widespread. "The probability that every single person in the United States is carrying drug-tainted money is almost certain," he said.

That kind of evidence could have a serious impact on the Justice Department's asset seizure and forfeiture program, which relies heavily on drug-sniffing dogs and laboratory tests confirming traces of drugs on cash, cars and other valuables. In 1990, Justice seized more than $176 million in assets—up from $17 million in 1986.

Graduates of the U.S. Customs Service Detector Dog Training Center at Front Royal, Va. (left) are detecting traces of cocaine on everyday items, bringing into question their usefulness.

Officials with the Drug Enforcement Administration and the Justice Department say they do not rely solely on the dogs anymore, but use them in conjunction with other techniques. "The Justice Department has been aware of this potential problem much longer than most defense attorneys have," said spokesman Dean St. Dennis. "That's why we use it with other factors, [such as] suspicious behavior."

Criminal defense attorneys say they have been arguing throughout the 1980s that convictions and search warrants should not be based on trace amounts of drugs. "What's new is that judges are starting to believe us and rule in our favor," said Atlanta criminal defense attorney Don Samuel.

Another judge who ruled for the defense, U.S. District Judge Thomas Wiseman of Nashville, declared on April 21 that "the evidence of the narcotic-trained dog's alert to [tainted] currency is of extremely little probative weight." The judge ordered all charges against the defendant dropped and $9,000 taken from him in an airport search returned. *Jones v. DEA*, No. 3:91-0520.

"It cannot be doubted that contaminated currency is widespread," Wiseman wrote. "The presence of trace narcotics on currency does not yield any relevant information whatsoever about the currency's history."

Studies Surprising

A number of studies support Wiseman's statement. Perhaps the most dramatic was conducted in 1985 by the *Miami Herald*. The paper asked 11 prominent local citizens to supply a $20 bill for testing. Among those who agreed were the Catholic archbishop; the state attorney, Janet Reno; then-first son Jeb Bush; former Miss America Kylene Barker Brandon; and the Broward County sheriff, Nick Navarro.

The surprising results: Ten of the 11 bills were tainted by significant traces of cocaine. Only Navarro's money was clean.

"Originally, the drug contamination on dollar bills was limited to Florida, but now it's everywhere," said Woodford. He points to a 1989 experiment by Dr. William Hearn, a Miami toxicologist, in which he gathered 135 dollar bills from banks in 12 cities across the country. Incredibly, only four of the 135 bills showed no traces of cocaine.

In 1987, a study by a DEA scientist found that one-third of all money at the Federal Reserve Building in Chicago was tainted with cocaine. His report, which had remained secret until this year, said traces of cocaine were found on the agency's high-speed sorting equipment and that the drug probably was being transferred to the currency.

"We recommend that trace analysis of currency for general enforcement or seizure be stopped," the report stated. But defense lawyers say the recommendation has not been followed.

"The use of drug-sniffing dogs has actually proliferated in recent years," said Albuquerque, N.M., lawyer Nancy Hollander, president of the National Association of Criminal Defense Lawyers. "These dogs are everywhere. They are at every airport, bus stop and train station."

Added Samuel: "No one is saying that these dogs are not smelling drugs. The point is, their smell is too good and they're smelling drugs on everything. If cocaine is on 70 percent of all the U.S. currency, and that is the latest estimate, then that should be the end of drug sniffs."

—*Mark Curriden*

 American Bar Assoc. Journal. ABAJ/LISA BERG

EXHIBIT 9

SCIENTIFIC AMERICAN

Permanent Address: http://www.scientificamerican.com/article.cfm?id=cocaine-contaminates-majority-of-american-currency

Cocaine Contaminates Majority of U.S. Currency

And it's not just the U.S.: Canada and Brazil have a preponderance of the drug powder on their bills, too

By David Biello | Sunday, August 16, 2009 | 30

COKED UP CURRENCY: An average of 90 percent of 234 U.S. banknotes of varying denominations tested positive for traces of cocaine in a new study.
Image: © American Chemical Society

For cocaine users, a rolled up $20 bill may be the most convenient tool for snorting the powder form of the drug. Or so it would seem from a new analysis of 234 banknotes from 18 U.S. cities that found cocaine on 90 percent of the bills tested.

Perhaps that's not surprising given that the U.S. Office of National Drug Control Policy reports that more than 2 million Americans used cocaine in 2007, which has been linked to ill effects ranging from debilitating addiction to heart attacks. The United Nations Office on Drugs and Crime, for its part, reported in the same year that 6 million Americans admit using cocaine annually, consuming a total of as much as 457 metric tons in a year.

"Cocaine is a powerfully addictive stimulant and one of the most commonly abused illicit drugs in the world," says chemist Yuegang Zuo of the University of Massachusetts Dartmouth, who conducted the tests and presented the findings today at the biannual meeting of the American Chemical Society, which is taking place in Washington, D.C. That city ranked highest in the survey—95 percent of the sampled bills there bore cocaine contamination—along with Baltimore, Boston and Detroit. Salt Lake City had the lowest average levels of contamination. "The examination of cocaine contamination on paper money can provide objective and timely epidemiological information about cocaine abuse in individual communities," Zuo argues.

What might be more surprising is the fact that the percentage of contaminated bills seems to be rising; just two years ago, Zuo did a similar study that found cocaine on only 67 percent of banknotes in Massachusetts. "It is too early to draw a conclusion about why," Zuo says. "The economic downturn may partly contribute to the jump."

But the U.S. Drug Enforcement Administration (DEA) notes that other measures, such as pretrial urine samples from defendants accused of crimes, show that drug use, at least in the D.C. area, has gone down slightly—only 29 percent of adult arrestees had traces of cocaine in their urine in the first six months of 2009, the lowest level since 1985. "We know that cocaine prices have gone up significantly in the last two years, which usually deters use of that drug," says special agent Melissa Bell of the Washington, D.C., division office of the DEA. "Junkies go on to use something cheaper."

Levels of cocaine ranged from .006 micrograms to more than 1,240 micrograms—the equivalent of 50 grains of sand—on U.S. bills, and $5, $10 and $20 bills on average carried more contamination than $1 or $100 bills.

Zuo and his colleagues also tested banknotes from Brazil, Canada, China and Japan, and found that Asians appear to use the drug less—only 20 percent of the 112 Chinese renminbi notes tested had traces, and only 12 percent of 16 Japanese yen notes tested bore the drug.

But Canadians seem to be just as fond and, perhaps, a bit sloppier in their consumption or dealing. More than 2,350 micrograms of cocaine were found on some of the Canadian bills, 85 percent of which had some level of contamination, while 80 percent of Brazilian reals also bore traces of the drug.

Whether this means drug use is on the rise or that ATMs and other bulk cash-handling machines—where one contaminated bill can spread powder to many others—are ever more ubiquitous cannot be discerned. "It is still difficult to tell quantitatively how much is due to primary contamination, such as during a drug deal or [use], and how much is due to secondary contamination, such as interaction between contaminated and uncontaminated bills," Zuo says. "Both may contribute ... [but] it seems clear that the banknotes containing 1,240 micrograms of cocaine were used directly during a drug deal or uptake [drug use]."

Previous studies, stretching as far back as 1987, have found varying levels of cocaine contamination, some even higher than the new finding. But Zuo is the first to analyze foreign banknotes for contamination and the first to employ a new method of gas chromatography, which detects the chemical signature of the drug without damaging the actual money, to do the analysis.

The finding might complicate an anti-drug dealing tactic used by the Federal Bureau of Investigation (FBI) and other enforcement agencies, Zuo says. In some cases, the FBI compares the levels of cocaine contamination on seized bills to levels found on bills in general circulation, treating this as evidence. "Sometimes [drug dealers] use these studies to try to get their money back when we seize it," Bell notes. But the DEA's drug-sniffing dogs are not actually detecting cocaine; they are sensing a chemical used in its manufacture that dissipates more quickly. "So they don't get their money back," Bell says.

Regardless, it would seem, according to this research, that C-notes are not as popular with drug dealers (or users) as perhaps popularly depicted. "You rarely see them breaking out the hundreds unless they're buying kilos," Bell adds. "The user on the street is going to be breaking out the five, ten or twenty."

EXHIBIT 10

The Criminal Practice Report

Published by Pike & Fischer, Inc., a subsidiary of The Bureau of National Affairs, Inc.

Volume 12, Number 23 November 18, 1998

Highlights

Practice Aids

Chemical, Dog Experts Debunk Debunkers of "Contaminated Money Myth"

The DEA hails Drs. Kenneth Furton and Stefan Rose, Miami, for "effectively" refuting the findings of many judges, based on testimony that high percentages of U.S. currency bear trace amounts of cocaine, that dog alerts to currency alone fail to establish probable cause for purposes of searches and seizures or forfeitures. They say the trained dogs they tested only alerted to bills heavily spiked with the "pseudo-cocaine" methyl benzoate, a by-product of street cocaine which they claim evaporates from exposed bills within two hours, meaning that alerts to money in the field indicate its recent proximity to bulk cocaine. Dr. James Woodford, the chemist who patented pseudo-cocaine, recounts his test demonstrating that if Furton and Rose had used circulated money, the odor would not have dissipated quickly. And dog experts Dr. Daniel Craig and Steven Nicely offer additional criticism of the revisionists' work. The Practice Aid includes excerpts from the Floridians' report and the DEA's March 1998 canine interdiction guide. (**Page 461**)

As Reciprocal Discovery Widens, So Does Need to Protect Consulting Expert

The trend toward reciprocal discovery in criminal cases has begun encroaching upon the hallowed ground of experts consulted in preparation for trial. For instance, after the defense was ordered to reveal the name and opinions of a consulting expert, the prosecution called him as an expert witness and revealed to the jury that he had first been retained by the defense. An attorney and psychologist offer advice on the most effective means to guard against this pernicious scenario. (**Page 471**)

Cross-Examination Can Waive Protection of Proffered Admissions

In plea negotiations, the defendant admitted to an unusual means of delivering a bribe to the mayor (palming the golf ball that he seemed to extract from the cup on the ninth hole green, making the mayor's son the winner of a hole-in-one contest and $40,000) but no plea bargain resulted. At trial, the defendant did not testify, assuming that his admission would be inadmissible under Fed.R.Crim.P. 11(e)(6) and Fed.R.Evid. 410. But on cross-examination of prosecution witnesses, his attorney asked questions that the U.S. Court of Appeals for the Seventh Circuit found presented a position contrary to that of the government, thus fulfilling the condition of his written waiver of protection for the admissions. (**Page 475**)

Also in This Issue

(continued on next page)

Who Really Knows What a Dog's Nose Knows?

In the materials on cross-examination in dog sniff cases excerpted in our last issue (*Something May be Rotten in the State of Drug Detection*, 12 CrimPracReport 444 (11/4/98)), Wichita attorney Daniel Monnat noted with a "caveat" Miami chemist Dr. Kenneth G. Furton's claimed refutation of the findings of the ubiquitousness of cocaine-"contaminated" currency in this country that have prompted many judges to discount drug detection dogs' alerts to money that was not found in immediate proximity to bulk cocaine. Furton's own findings may prove to be at best a mixed blessing for prosecutors, however.

Furton's testimony in three federal court proceedings indicates that, at least as of last December, his research, described in a report excerpted below, has not been subjected to peer review and has not been described sufficiently to permit replication of the results by others. Thus, it may be challengeable on its face under *Daubert v. Merrell Dow Pharmaceuticals, Inc.*, 509 U.S. 579 (1993), to the extent the judge is inclined (at a pre-trial hearing) or required (at trial) to follow the Federal Rules of Evidence. Also, as discussed below, several particulars of Furton's reported methodology and findings are disputed by drug detection experts Dr. Dan J. Craig, San Antonio, Tex., and Dr. James Woodford, Brentwood, Tenn., as well as by Steven D. Nicely, a San Antonio dog trainer. Indeed, lawyers can obtain from Woodford an "Olfactory Test Kit" (described below) that they can use as demonstrative evidence, in Woodford's words, to "refute Furton's claims" in the courtroom.

Furton contends that alerts by trained dogs to paper money necessarily indicate the bills' recent proximity to a large quantity of cocaine because the dogs in his tests could not detect pure cocaine in amounts less than one gram, meaning that the presence of trace amounts on bills is irrelevant, and because the dogs could only detect bills spiked with a relatively high level of the synthetic chemical by-product of cocaine, the "pseudo-cocaine" methyl benzoate, which Furton says is "highly volatile" and dissipates quickly in open air. Ironically, this raises questions about the reliability of many alerts that law enforcement authorities and judges have credited.

"So what" if there's drug odor? Indeed, Nancy Hollander, of Freedman, Boyd, Daniels, Hollander, Goldberg & Cline, Albuquerque, rhetorically asked the *Report* how probable cause can exist if a dog cannot distinguish between drugs actually present and a mere odor, easily absorbed, that may have been picked up innocently. As she remarked,

> It is not illegal to drive a car that once contained illegal drugs. It is not illegal to put your purse or suitcase in a locker that once contained illegal drugs. A dog alert may be probable cause that the odor of drugs is present, but so what? Being in proximity to the odor of drugs is not a crime. This, to me, is the fundamental evidentiary problem with the dogs, which cannot be cured. That is why I believe the entire dog-sniff program is a mere subterfuge to maneuver around the requirements of the Fourth Amendment.

The DEA's current *Guide to Canine Interdiction*, published last March (excerpted below), asserts that the "contaminated currency myth" has been "effectively" refuted by Furton and his colleague, Stefan Rose, M.D., and recommends use and dissemination of their findings. At the same time, however, the guide admonishes that dogs should not be trained at facilities that use the "pseudo-cocaine" methyl benzoate, lest they be trained "away from the drugs and onto the pseudo substances." Furton and Rose admittedly used only pharmaceutical grade cocaine and methyl benzoate in their tests—no "street cocaine" and no circulated currency, which are what drug detecting dogs in the field are supposed to alert to.

Also, as Hollander points out, the guide suggests that where "no substance is located" following an alert in the field, the dog's handler should attempt to validate the alert and protect the dog's reliability record "by developing evidence that a controlled substance was at one time present in the vehicle, box or suitcase to which the canine alerted," or by eliciting a traveler's admission of recent drug use. The recommended technique for doing so—simply asking if the person can explain why the canine alerted—is premised on a recognition that such "corroborating" circumstances will not support a prosecution but will salvage only the dog's reputation. Thus, the DEA, together with Furton and Rose themselves, may have provided adversaries with potent ammunition for attacking their findings.

In fact, Martin J. Bidwell, an assistant federal public defender in the Southern District of Florida, recently had little difficulty persuading a judge that *Daubert* required exclusion of Dr. Rose's proffered testimony that the methyl benzoate emanating from $42,000 in cash, found in a defendant's car trunk some eight months after the purportedly related drug transaction, could have survived that long in the container (a small leather-look kit bag) in which it was stored and to which a dog alerted shortly after the seizure. *U.S. v. Gerrow*, SDFla, No. 97-6051-CR-GOLD, Snow, C.M.J. Bidwell told the *Report* that Rose's tests simply failed to address the conditions presented by the case, including the permeability of the container, heat and other possible environmental variables in the trunk, and the purported duration of the storage.

> **"No scientifically controlled study has been conducted to determine if dogs trained on one [street cocaine or pseudo-cocaine] can detect the other."**

Absence of peer review and replicability. In *Daubert*, the Supreme Court said that in performing its role as "gatekeeper" against admission of unreliable (and hence not "relevant") scientific testimony, the trial court should conduct a "flexible" inquiry, considering the following factors: (1) whether the theory or technique can be (and has been) reliably tested; (2) whether it has been subjected to peer review and publication; (3) its known or potential error rate; (4) the existence and maintenance of standards controlling its operation; and (5) whether it has attracted widespread acceptance within the relevant scientific community.

On Dec. 2 and 4, 1997, Furton testified for the government in *U.S. v. $201,700 in U.S. Currency*, SDFla, No. 97-73-CUV-SH. Direct examination on both days covered the extent to which his research has been published; the following excerpt is from the transcript of Dec. 4, pp. 7-8:

> Q. Have you presented your research findings on odor detection by narcotic detector dogs to the scientific community?
>
> A. Yes, I presented it at approximately ten different conferences over the last five years.
>
> Q. Have your research findings on odor detection by narcotic dogs been published?
>
> A. Yes, one of the conferences I attended was in Boston last year and they published the conference proceedings. It is one of the chapters in that proceeding. . . .
>
> Q. What's a conference proceeding?
>
> A. The conference proceedings are similar to book chapters in that you have like an editorial board that will edit the book for the conference proceedings versus a journal article [that] typically gets sent out for peer review by other scientists. Based on the review a monthly journal will publish the work.
>
> Q. What does the peer review proceeding involve?
>
> A. It is usually anywhere from two to three scientists within the same research area will review the work and then make recommendations on whether it should be published at all, whether it should be published in that particular journal. . . .

Thus, the transcripts suggest that Furton has not even claimed that his work has passed peer review. In an interview with the *Report* concerning the DEA's guide and Furton's findings, as set forth in his testimony and in an undated report Furton has distributed with his curriculum vitae, animal behavior consultant Dr. Dan J. Craig, a veterinarian with a master's degree in experimental psychology, said that the research also has not been reported in sufficient detail to permit its replication by others. For example, he noted, Furton does not reveal how the dogs in his study were trained, and whether they were trained exclusively on street cocaine or on pseudo-cocaine. Craig said he knows both substances have been used by dog trainers and that "no scientifically controlled study has been conducted to determine if dogs trained on one can detect the other."

Potential for error demonstrated by Woodford. Furton's report and testimony do not directly address the known or potential error rate in his and Rose's work. However, Dr. James Woodford, a Ph.D. in chemistry who in 1981 was granted the patent for "Odor of Cocaine," the pseudo-cocaine methyl benzoate, and whose formulation of it was tested in the 1979 U.S. Customs dog proficiency training studies, told the *Report* of a number of ways in which he believes Furton's work is flawed. He said that our initial inquiry prompted him to conduct an experiment on the volatility of methyl benzoate on paper money. On Nov. 11, 1998, at 9:00 p.m., he said, he took a circulated one dollar bill from his wife's purse, spiked it with 10 micro liters of methyl benzoate (the same amount Furton and Rose used per bill), and placed it uncovered outdoors, in a constant wind of about five m.p.h. and at temperatures between 40 and 65 degrees Fahrenheit. Thirty-six hours later he could still smell the methyl benzoate well enough to

pick the bill out blindfolded from an array containing 10 unspiked bills.

How could he do this if Furton's dogs could not smell the same substance on his bills after two hours, which supposedly proved that dogs only alert to bills that have very recently been near cocaine? One reason is that Furton used uncirculated bills and washed them in methanol to boot, according to Woodford. Furton said the washing was to ensure that no trace cocaine was present, but Woodford questioned the need to do that if the money was really uncirculated. He explained that circulated money contains "sebum, a thick, viscous golden, and oily liquid," up to 50 milligrams per bill, which he calls (in a take-off on the perfume industry's name for methyl benzoate, "Oil of Niobe") "Oil of Money." And he spelled out how Oil of Money is the key to the retention of odors in bills:

> The more the money has circulated the more sebum it picks up and holds inside the bill. Oil of Money, when isolated in a flask, has a strong balsamic odor. It is a collection of fingerprint oils, sweat, etc. Cocaine, marijuana, opiates, methamphetamine and other many other drugs as well as their associated drug odor dissolve in Oil of Money. The oil acts like an encapsulator of odor. It retains drugs and their associated odors over long periods of time. Days, weeks, months, even years. Changes in temperature and humidity will cause Oil of Money to release odors from time to time. Methyl benzoate dissolves in this oil and will remain dissolved for long periods of time. Years if sealed in plastic. I opened up a packet I've stored since 1978 and it still smells strongly of methyl benzoate. When you wash or launder money with methanol you remove the Oil of Money. If you apply methyl benzoate to non-laundered money, that is, money from general circulation, the methyl benzoate gets captured and retained in the Oil of Money.

Referring to his current experiment, Woodford said, "I estimate it could take many days, maybe a month or more, depending on the humidity and temperature and packaging, for my spiked bill to lose enough methyl benzoate odor from the Oil of Money in the bill to fall below the femtogram range (1×10^{-15}) that a trained dog should be able to detect."

Drug detection expert Craig said he found Furton's research flawed in that he apparently did not test how much methyl benzoate bills will absorb when not spiked with it but merely placed near bulk quantities of street cocaine. He did not comment on Furton's washing of the bills, but his general admonition is apt: "Tests have to be tailored to the real world." The criminal justice system is concerned with street cocaine and circulated money, and Furton's reported tests involved neither.

Objective tests, certification standards needed. The dog sniff study by Furton and Rose evidently was not a disinterested, purely scientific undertaking. On Dec. 2, 1997, in the Florida case cited above, Furton testified on cross-examination that Rose suggested the study while serving as the director of the University of Miami's forensic toxicology lab, where he was involved in forensics testing of "all the evidence" for the Metro-Dade Police Department. The study was not officially commissioned by the police, according to Furton, but he acknowledged that one police officer coordinated the participation of all the dogs in the tests, and in Furton's and Rose's promotional package for their enterprise, University Medical and Forensic Consultants, Inc., the estimated fee for work on a case involving a dog alert to currency is $8,000 (32 hours at $250 per hour). Given that their findings will generally support forfeiture actions, they will be hired by the prosecution rather than by the defense in practically every case.

Steven D. Nicely, a former police officer, is a professional dog trainer who has been working with drug detector dogs since 1973 and is an admirer of Craig's work with them. He told the *Report* he is available to testify for either side and that his primary interest is to "improve the profession." He says he fears that the flawed nature of Furton's work and the DEA's endorsement of it may endanger the future utility of drug detection dogs. His primary criticism, like Craig's, is that Furton says nothing about how the dogs he used were trained and seems ignorant of what a "properly" trained dog can and cannot really do. Nicely says that if the dogs used in Furton's tests were trained on methyl benzoate (he suspects that they were if they came from U.S. Customs), it was like conducting a chemical experiment with a "contaminated beaker."

Nicely recounts training six drug detection dogs in about 1990 on street cocaine, in amounts ranging from one gram to one ounce, and not using any methyl benzoate in their training. (As noted above, training only on drugs is recommended in the DEA guide.) When another trainer, unaware of how the dogs were trained, put out methyl benzoate for them to alert on, they did not respond. Nicely says this disproves the theory that all the dogs smell from the cocaine is methyl benzoate. He also points out that law enforcement agencies have a strong conflict of interest that arises from potential currency forfeitures—they receive shares of forfeited funds. This fact gives them a disincentive to question Furton's seemingly helpful conclusions, which may backfire.

In Nicely's opinion, the Department of Defense has the resources and the objectivity to conduct a truly scientific study of the issues in chemistry, physics, and human and animal behavior that are presented by dog sniff evidence, and such a study is the only hope for reliably resolving those issues. Meanwhile, he says, courts should demand more proof for all claims regarding such evidence, and perhaps the case law, largely based on unsubstantiated assumptions and assertions, should be "scrubbed." He points out, for example, that the "certifications" of drug detection dogs advocated by the DEA and relied upon by many courts are meaningless without proof of what is required for certification, which varies greatly from agency to agency. A uniform national standard of certification is needed, he says. Another problem area in Nicely's

view is the behavior of human trainers and handlers, who can unconsciously cue their dogs and should be tested for such conduct and trained to avoid it.

Oil of Money smooths courtroom test. Woodford does not echo Nicely's point that dogs trained on street cocaine alone will not alert on pseudo-cocaine. In fact, Woodford believes that dogs alerting to cocaine primarily smell methyl benzoate, and he suggests that Furton and Rose should give him credit for discovering that fact, which he says is documented in his patent, instead of acting as though they discovered it. Noting that his patent expired last April, he says, " My 17 years are up. Now they attack!" But he launches the following counterattack, sent to us by e-mail:

> My comments and suggestions on how defense attorneys can challenge Furton under the Daubert case's standards of scientific reliability: they can test (Proof) the dog's capabilities. I have Olfactory Test Kits available for attorneys to use in Court as demonstrative evidence to refute Furton's claims. I've spiked circulated (not washed) dollar bills with 10 micro liters (same amount they use) of methyl benzoate and sealed them in zip-lock type plastic. Lawyers can use these Kits in forfeiture proceedings whenever Furton, Rose and their colleagues show up to help DEA mislead the gatekeepers of science (Judges). With the test kit as a trial aid, a lawyer can ask the jury or judge attempt to smell detect the methyl benzoate through the plastic wrapping. Furton says the odor passes right through plastic. When the lawyer scissors open the plastic wrapping and reveals the bill, it smells clearly to everyone in the courtroom. The idea then is to place the spiked bill in an empty courtroom or place where it is far away from the jury's noses. The lawyer asks the judge to allow the jury to periodically go into the empty room and sniff the dollar bill. They can wait how-ever-long it takes until no jurors can smell-detect it. Furton and crew say it evaporates fast, "could be less than 2 hours." I spiked an unwashed, circulated bill at 9 PM (November 12, 1998). That was last night, now 25 hours ago, and it still smells clearly of methyl benzoate. With my Test Kit, the lawyer can demonstrate that their testimony is erroneous and misleading.
>
> The Olfactory Test Kit for defense Lawyers contains a small bottle of methyl benzoate and a 10 micro liter pipette so lawyers can do the spiking of whatever object they want to test and smell and wait for it to dissipate. After the money or object spiked with the methyl benzoate dissipates to the level where the human can't smell it then more waiting time is required for the level to fall down past where a dog could not smell it. . . .
>
> Yet another trial aid contained in the kit is a plain paper bag. Furton says, "A paper bag is better than a zip lock bag to contain the odor". My kit comes with paper bag. The lawyer uses the micro liter pipette to transfer 10 micro liters methyl benzoate onto the surface of an unwashed (generally circulated) dollar bill. Then puts the bill inside the paper bag. Ties the end with a twist-tie and lets the jurors smell it through the paper bag and compare the amount of odor with the spiked bill contained in the zip-locked plastic bag – which does not let the odor escape like Furton and his group says.

Although Nicely does not share Woodford's and Furton's convictions concerning the dominance of the methyl benzoate odor in dogs' nasal passages, he does agree with Woodford that dogs can smell far smaller amounts of cocaine odor than Furton claims. And he challenges Furton's contention that the dogs he used were trained to alert on no less than one gram of cocaine. He says, "You can't control a dog's threshold."

Other approaches, including the DEA guide. Theodore Simon, Philadelphia, a veteran in litigating dog sniff cases, has not yet seen Woodford's kit, but he has worked with the chemist and vouches for his knowledge and credibility. He told the *Report* that his first response, assuming that Furton's results could be replicated, would be to challenge the relevance of Furton's theory in practically all cases on the ground that he only used cleansed currency and methyl benzoate. In a case involving the seizure of anything other than cleansed money—perhaps in sealed Federal Reserve packets—the prosecution should not "get to first base" with Furton's testimony, says Simon.

Simon also reasons that since methyl benzoate occurs in legal substances, like perfume, an alert when no drugs are found proves nothing but the presence of methyl benzoate. When asked while testifying at a deposition whether a dog would alert to money doused with perfume, Furton said, "No. I don't believe that. I don't believe that K-9's are, properly trained K-9's will alert to perfume. I've never seen that reported and wouldn't expect it based on our studies." *U.S. v. $500,000 in U.S. Currency*, SDFla, No. 95-1222 CIV, Ungaro-Benages, J. (transcript of 1/29/96). In Furton's and Rose's "Typical Report" below, they say they are "familiar" with "perfume analysis" and give their "expert opinion" that a detection dog would not alert to perfume because the amount of methyl benzoate it contains is "so minute as compared to the hundreds of possible volatile substances" in perfume. The basis for their claimed expert knowledge of the selectivity of dogs' odor detection ability is not stated.

Nancy Hollander says that in drug sniff cases she has focused mostly on the inadequacy of the dogs' training and/or records. The DEA guide is potentially helpful in this area. As the excerpts below show, it makes specific recommendations about keeping thorough dog training and performance records, documenting all non-seizure alerts, as well as fruitful ones. The guide also obligingly provides defense counsel with the prosecutor's script for direct examination of a canine handler, which includes several questions suggesting the need for documentation of training and performance facts that might undermine the dog's "credibility."

Finally, the guide supplies a fact long unknown in the criminal defense community. As we noted in our last issue's discussion of dog sniff cases, 12 CrimPracReport at 447, 449, advocates of the contaminated currency theory have for some time supported their motions with copies of the undated Report on Trace Analysis of U.S. Currency by DEA forensic chemist Sanford A. Angelos of the North Central Laboratory. Appendix D to the guide, excerpted following the guide excerpts, is a memorandum on ionscan detection devices dated May 3, 1996, from DEA Deputy Chief Counsel Robert T. Richardson to Michael S. Connolly, Special Agent, Concord Resident Office. Richardson's memorandum, which refers to the report of the North Central Laboratory which "found drug contamination of a large percentage of the tested currency in general circulation," and "has been misconstrued by attorneys as supporting the proposition that all currency in general circulation is contaminated" (he does not state what the correct construction of the report would be), also refers to it by its date, July 12, 1985. That information may help to authenticate the document if it is needed in future cases.

Dr. Craig may be reached at 210 679-7804; Dr. Woodford at 615 221-6448; and Mr. Nicely at 210 521-5465. The number for the consulting company of Drs. Furton and Rose is 305 378-8436.

"TYPICAL REPORT" BY DRS. FURTON AND ROSE

Excerpt from the DEA Guide's Appendix E: "Typical Report" from front page of "Asset and Forfeiture information package for contaminated currency cases" by Kenneth F. Furton, Ph.D., and Stefan Rose, M.D., of University Medical and Forensic Consultants, Inc., Miami.

Based on our training and experience in the field of forensic science, the research we have conducted with narcotic detection canines and our review of the literature, it is our expert opinion that a positive alert to U.S. Currency by a properly trained narcotics detection canine indicates that the currency had recently, or just before packaging, been in close or actual proximity to a significant amount of narcotics, and is not the result of any alleged innocent environmental contamination of circulated U.S. currency by microscopic traces of cocaine.

"[I]t is our expert opinion that a positive alert to U.S. Currency by a properly trained narcotics detection canine indicates that the currency had recently, or just before packaging, been in close or actual proximity to a significant amount of narcotics, and is not the result of any alleged innocent environmental contamination of circulated U.S. currency by microscopic traces of cocaine."

Our research has included a study of more than a dozen different narcotics detection canines and their abilities to detect the odor of cocaine. It is our conclusion that narcotics detection canines actually alert to the odor of the chemical methyl benzoate, and not pure cocaine.

Methyl benzoate is a highly volatile substance associated with street cocaine which evaporates quickly when handled or exposed to air while pure cocaine hydrochloride does not evaporate and is transferred rather easily by physical contact.

We are also familiar with fragrance and perfume analysis and it is our expert opinion that the methyl benzoate found in some perfumes is so minute as compared to the hundreds of possible volatile substances contained in a perfume that a narcotics detection dog trained to alert to cocaine would not alert to perfume.

We are also aware of numerous non-alerts by trained narcotics canines to large amounts of circulated U.S. currency, a fact which supports our theories, and is inconsistent with the theory that all U.S. currency is contaminated with so much cocaine that narcotics detection canines will alert to circulated money innocently contaminated with cocaine.

REPORT ON ODOR SIGNATURE OF COCAINE

Excerpts from "Odor Signature of Cocaine Analyzed by GC/MS and Threshold Levels of Detection by Drug Detection Canines," a report by K.G. Furton, Y.-L. Hsu, T. Luo, J. Wang and S. Rose, Department of Chemistry, Florida International University, Miami (undated), included in package with Furton's and Rose's CVs.

.... Field tests on fifteen different drug detector dogs with varying breeds, ages and training regimes show a consistent threshold level of 1 μg of methyl benzoate spiked along with cocaine on US currency required to initiate an alert. The majority of canines did not alert to pharmaceutical grade cocaine even at levels as high as 1 g. Methyl benzoate is shown to evaporate rapidly from individual bills and is a function of the available surface area for wrapped currency. The canines tested were remarkably selective and reliable even under varying test conditions and using different delivery devices (i.e. large cardboard boxes and small metal cans).

.... [Reports "suggesting" contamination of all circulated money with trace amounts of drugs, including cocaine] have resulted in contaminated money theories purporting that [sic] due to this widespread contamination, any person carrying money could potentially initiate a drug dog alert. The legal significance of this theory ranges from reducing the probative value of drug dog alerts to the complete elimination of drug dog utility if, indeed, canines can alert to any sum of currency.

.... [Conclusions, reported in *U.S. v. $30,060*, 39 F.3d 1039 (CA9 1994), that 75 to 90 percent of all U.S. cash bears enough cocaine to alert a drug dog] are alarming in light of the fact that there are no definitive peer-reviewed studies demonstrating the "range of a drug dog's detection capability" to cocaine nor are there any statistically significant de-

terminations of the degree and extent of cocaine contamination on U.S. currency. Although the limited above mentioned studies indicate that there is widespread contamination of U.S. currency by detectable levels of cocaine, the actual levels and significance to drug detection have not been established with any degree of scientific certainty.

.... [Suggests that a statistically meaningful study of the "more than $440 billion in U.S. paper currency in circulation at any given time" cannot be extrapolated from "tiny sample sizes chaotically sampled from" different sites and regions, and that the limited lifetime of currency ("less than ca. 2 years") means that levels of contamination in given bills will vary depending on their age.] Thirdly, since it is clear that canines do not alert to a single molecule of a chemical but, rather, to significant concentrations of the chemical, additional studies are needed to confirm the threshold, range and specificity of canines to detect the volatile chemicals associated with cocaine before any general conclusions can be reached. A fourth major issue is that quantitative levels of volatile chemicals associated with cocaine and proven to elicit an alert by drug detection canines, such as methyl benzoate, have never been reported on paper currency. And finally, properly trained detector dogs have been shown repeatedly not to alert to circulated currency. [Footnoting fact that "Guilfoyle, T., Supervisor of the Forfeiture Section of the Metro-Dade Police department, is the custodian of 50 reports of non-alerts to currency. ED. NOTE: It does not appear from the report that the dogs tested came from anywhere but that same police department, and the report acknowledges that the department's Sgt. Wes Dallas coordinated the testing. Also, the report says nothing about what substances the dogs were exposed to in training, or whether their past reliability in detecting cocaine was documented. It appears from Furton's testimony that personnel and dogs from other agencies may have participated in the tests, but he did not discuss their training and past reliability.]

[Says that the only currency contamination tests reported in published research papers have not found "substantial levels of cocaine concentration on circulated currency."]

.... We have performed tests on fifteen different drug detector dogs with varying breeds, ages, and training regimes. U.S. paper currency was spiked with successively increasing amounts of cocaine and volatile cocaine by-products .... To date, the only chemical found to produce consistent drug dog alerts has been methyl benzoate. ....

Our results indicate that drug detector dogs alert to the common volatile cocaine by-product, methyl benzoate rather than to the cocaine itself. None of the dogs alerted to by-products other than methyl benzoate and the **majority did not alert** [emphasis in original] to synthetic "pure" cocaine even at the highest levels tested of 1 g. . . . The "pure" cocaine standards we obtained from commercial sources were found by GC/MS to be contaminated with small amounts of detectable impurities including methyl benzoate. The finding that methyl benzoate, rather than the cocaine itself, is responsible for alerting drug detector dogs is not surprising given our current knowledge of how detection dogs alert to forensic specimens. When a dog is trained to alert to an item such as a human body, explosives, munitions, accelerants, drugs, currency, etc., the canine is actually being trained to alert to a scent associated with the item rather than the item itself. That scent is composed of volatile compounds or classes of compounds which are detected by the canine in the gaseous state. This is the basis of commercial training aids developed, such as pseudo cocaine, pseudo heroin, etc. which, in fact, contain no controlled substances but, rather, only the controlled substance odor.

It is well established that canines have a remarkably selective sense of smell, that is, they can be trained to alert to the volatile chemicals associated with the detection material even in the presence of numerous potentially interfering compounds. It is also known that canines can be trained to alert only to specific threshold levels of chemicals. Our studies indicate that the levels of "pure" cocaine (which always contains finite levels of impurities including methyl benzoate) required to signal an alert for the dogs tested are extremely large.

.... We have established that the threshold level of detection of a pharmaceutical cocaine for the canines as tested is greater than 1 g. (containing $< 0.001\%$ methyl benzoate impurity) with a consistent threshold level of methyl benzoate of around 1 μg.

These levels of cocaine are orders of magnitude higher than the < 10 μg./bill average solvent extractable cocaine reported for U.S. currency in circulation [citing "'Crime and Chemical Analysis,' in Research News, *Science*, 24 March 1989, p. 1555"], and methyl benzoate, the chemical marker, has not been reported on circulated currency. Additionally, the amount of cocaine on the *surface* of circulated bills is likely several orders of magnitude less than that which is solvent extractable (ca. < 10 ng./bill) [citing "Jourdan, T.H., FBI, Personal Communication"]. Methyl benzoate evaporates rapidly from the surface of single dollar bills ($> 90\%$ evaporates in 120 minutes) but evaporates more slowly when contained within a stack of bills together ($< 10\%$ evaporates in 120 minutes when 30 bills thick). In conclusion, there is no valid scientific basis for the theory that innocently contaminated currency contains sufficient quantities of volatile chemicals to signal an alert from a properly trained drug detector dog. Therefore, an alert to a specimen (including money) by a properly trained drug detection canine indicates that that item contains a significant quantity of narcotic odor. . . .

1998 DEA GUIDE TO CANINE INTERDICTIONS

Excerpts from "A Guide To Canine Interdictions: Maximizing the Impact of Drug Scent Evidence," *published in March 1998, prepared by Richard A. Medema, Staff Attorney, Drug Enforcement Administration, Office of Chief Counsel, Asset Forfeiture Section, P.O. Box 28356, Washington, D.C. 20038, (202) 307-7648.*

We generally delete the guide's footnotes, which contain numerous case citations, including summaries of holdings.

Introduction

. . . .

Historically, an alert by a drug canine has provided the probable cause necessary to search or arrest, and the drug connection necessary to justify seizure and forfeiture of property pursuant to 21 U.S.C. § 881. In recent years, however, while generally accepting the admissibility of the evidence, courts are challenging the weight to be afforded the canine's testimony [sic]. Courts are generally reluctant to consider the fact of the canine's alert as conclusive proof of the guilt of the defendant or of the forfeitability of property. While some recent decisions have acknowledged the positive canine alert as a factor supporting forfeiture, other significant factors have been present in these cases to link the currency to drug trafficking.

In addition, a court is not likely to give the handler's testimony great weight unless the canine and its handler are certified as experts in detecting the odor of controlled substances. The courts will, therefore, allow the defendant/claimant wide latitude to cross-examine the canine [sic] at its weakest link—the handler. An effective cross-examination of the canine's training, and the handler's technique and record-keeping can impact negatively on the reliability of the canine—all factors which again go the *weight* to be afforded the canine's testimony. It is crucial to sustain this testimony because in many cases, particularly where a search of a vehicle is involved, the court will be deciding the appropriateness of a subsequent warrantless search based primarily upon the canine's alert. Where the court determines the canine is not a reliable witness, the evidence will be suppressed and the property will be ordered returned.

"This guide is designed to suggest ways the canine handler and prosecutor can strengthen the impact of canine alert 'testimony' in court."

This guide is designed to suggest ways the canine handler and prosecutor can strengthen the impact of canine alert "testimony" in court. Each time an alert is made, the handler should be prepared to document and describe that alert in court. The prosecutor, likewise, should expect a defense challenge to a positive canine alert and should be prepared to meet that challenge. . . . This guide is not a statement of standard operating procedures, nor is it to be inferred or implied that a canine handler has been deficient in any respect for not operating in a manner consistent with the suggestions set forth in this guide.

[Lists four topic areas in Guide.] The opinions and recommendations contained in the "Training" section have been provided by an informal panel of some of the most knowledgeable canine handlers in the country today. [ED. NOTE: The panelists are not identified.]

1 Training

[The marketplace has responded to increasing demands for "drug canines"] by providing canines which have been trained by a wide variety of methods and with varying degrees of success. . . . It is recommended that a canine be acquired which will be trained with the department handler as a team, instead of purchasing a "pre-trained" canine and pairing it with a handler. The advantage . . . is that the handler learns to direct and "read" his canine, and the canine learns how to respond to the handler, and is not allowed to develop any bad habits in the training process. In addition, the trained team should be certified by an organization that has no financial interest in the training process.

Departments . . . should select a facility which trains canines to alert to the scent of controlled substances, rather than pseudo-controlled substances. It has been demonstrated that an experienced canine will not alert to methyl benzoate, a commonly used "pseudo-cocaine." Training with the pseudo-substances may train the canine away from the drugs and onto the pseudo substances. Initial training [also] should avoid training with masking agents in the same location as the controlled substances because of the risk of contamination and the creation of incorrect association in the canine with the masking agents.

[Recommends exposure of dogs in training to varying amounts of drugs.] Ultimately, a canine will alert to the level of controlled substance consistent with its training.

[Warns against "any unorthodox action" in training which might give "the shrewd defense lawyer" the means to challenge the dog's reliability.] Since the canine cannot testify as to what it is alerting [to], a canine which is trained to detect anything in addition to controlled substances provides the opposing party the means of diminishing the reliability of the canine's alert. [Further suggests that a dog handler should not have to explain more than one "type" of alert for controlled substances, "particularly in a situation where the canine has found currency."] The canine should be trained to alert in one manner, and that manner should remain consistent throughout the canine's career.

. . . .

1.4 Certification and Recertification

It is imperative that the canine be recertified on an annual basis at the facility which originally trained the canine, or a comparable facility which has a recertification program. The agency involved in the recertification should be a neutral, objective third party with **no** involvement in the continuing training of the canine. [Emphasis and apparent inconsistency in original.] The recertifying official should be qualified to testify as an expert witness in the field of canine training. Voluntary state associations of law enforcement officers

should consider establishing a recertification program for the benefit of their members who are canine handlers.

2 Effective Operation of the Drug Canine

. . . .

2.1 Documentation

[Warns that "[o]ne of the greatest areas of attack" on drug sniff testimony is the lack of complete documentation of the dog's "professional life, including records detailing training, certification, and operational history, and recommends administrative support and encouragement for handlers' record keeping.] Courts have ordered canine records produced to allow a defendant to prepare a cross-examination of canine handlers, and have entertained motions to suppress drugs found by canine alert where allegations that the handler's inconsistent testimony and inadequate record-keeping were raised. [Citing *U.S. v. Florez*, 871 F.Supp. 1411, 1422, 1424 (DNM 1994) (Defense counsel Nancy Hollander brought out four false alerts that were not recorded in the reports produced, and court commented on the insufficiency of the handler's memory alone and said, ". . . [W]here records are not kept or are insufficient to establish the dog's reliability, an alert by such a dog is much like hearsay from an anonymous informant . . .")]

[Recommends documentation of all a dog's alerts, including brief descriptions of circumstances.] A current, concise, legible canine ledger will reinforce the handler's professionalism before the trier of fact, as well as serving as a testament to the canine and canine handler's success. In many cases, the presence of a properly-maintained log will spell the difference between winning or losing at trial. The key to establishing the reliability of the canine is documentation of the canine's performance record. [Appendix A to the Guide contains a sample monthly report on the dog's performance.]

"The report of even the most reliable canine may be discounted by the court which does not believe that a canine alert, standing alone, provides the drug connection necessary to establish probable cause for forfeiture pursuant to 21 U.S.C. § 881."

[The next two subsections discuss the need for regularly keeping training and search and seizure records, including records of any non-contraband substances the dog encounters on the job, such as masking agents. Appendix B is a sample "Drug Canine Alert Report."]

2.1.3 Currency testing records

. . . . Documenting those instances in which a canine alerts [to currency] is essential in demonstrating that the canine can detect controlled substances. Conversely, documenting those operational instances in which currency is placed in a neutral location for the canine's examination, and where the canine does not alert, is especially critical to counter the popular and unsubstantiated theory that drug canines are actually alerting to the smell of the currency itself, or that the contamination of currency in general circulation with drug residue triggers a canine alert to all currency. In addition, the canine handler should conduct periodic canine examination of currency drawn from local banks as an additional tool in countering the contaminated currency myth. Appendix C contains a "Non-Seized Currency Log" on which to document those canine inspections of currency drawn from local banks. The use of previously circulated, shredded currency from the Federal Reserve is not recommended because excessive chemical saturation might be present on those shredded bills and might in fact have necessitated removal of the bills from circulation. The risk that such contamination might trigger an alert should be avoided at all costs.

2.2 Corroboration of Canine Alert

2.2.1 Following seizure of currency

The report of even the most reliable canine may be discounted by the court which does not believe that a canine alert, standing alone, provides the drug connection necessary to establish probable cause for forfeiture pursuant to 21 U.S.C. § 881. [Citing *U.S. v. $5000 in U.S. Currency*, 40 F.3d 846 (CA6 1994); *U.S. v. $67,220 in U.S. Currency*, 957 F.2d 280 (CA6 1992); *U.S. v. $80,760 in U.S. Currency*, 781 F.Supp. 462 (NDTex 1991); and *U.S. v. $30,060*, 39 F.3d 1039 (CA9 1994).] An attempt should therefore be made to corroborate the canine alert by the collection of drug residue through an Ion Mobility Spectrometer (IMS) "Ion Scan" or Illicit Substance Detector (ISD) sweeping of the area to which the canine alerted, the container in which the currency was carried, the pockets and hands of the courier, and the interior of any luggage carried by the courier and their companions. . . . A memorandum concerning the use of Ionscan detection devices within the Fourth Amendment context and asset forfeiture context is attached as Appendix D. The testing protocol employed by the [Dallas-Fort Worth] airport task force is available from the author upon request.

2.2.2 Following non-seizure alert

The handler should be prepared to document instances in which an alert is made but no substance is located. An effort should be made to corroborate the canine alert, to counter any suggestion that the canine has made a false alert by developing evidence that a controlled substance at one time was present in the vehicle, box or suitcase to which the canine alerted. This corroboration may be achieved by simply asking the traveler if they could explain why the canine alerted. If asked, the traveler may acknowledge prior drug usage by "friends" to explain the canine alert on their luggage. [Citing *U.S. v. Diaz*, 25 F.3d 392 (CA6 1994), where passenger's statement that clothing may have retained odor of marijuana smoked "all weekend" "adequately explained the 'false positive' alert."]

[Suggests use of IMS or ISD scans and/or communicating with government data bases "for information which ties the traveler to drug trafficking" to corroborate valid basis for "false positive" alerts. Reminds handlers to "validate" even those alerts in reports such as the sample in Appendix B, which asks whether laboratory analysis, a data base screen, or other corroboration has been obtained where dog alerted but no drugs were found. Cites *Florez* opinion, 871 F.Supp. at 1422-23, on the importance of such measures.]

2.3 Proofing

[Discusses the need to test the dog periodically, or "proof" it, to make sure that odors from non-controlled substances, such as tape, plastic, dryer sheets, or the chemicals in all currency—present alone in non-circulated, shredded currency obtainable from a Federal Reserve Bank—are not triggering the dog's alerts.]

2.4 Degradation analysis

Lawyers contesting forfeitures have introduced evidence of chemical analysis which suggests that a percentage of currency in general circulation may be contaminated to some degree with microscopic particles of controlled substances. This analysis has not established, however, that a canine will therefore alert to all contaminated currency. Many canine experts have long believed that the canine alerts, not to the individual micrograms of controlled substance on the currency, but to the scent of drugs, which is a combination of many factors. Those factors which impact the canine alert include the length of time the currency has been packaged with or in proximity to the controlled substances, the amount of the controlled substances, and the method of packaging the currency. The length of time the scent will remain on currency is subject to many variables, including the environment.

This is precisely the conflict which prompted the pivotal 1996 study of drug canine behavior by Drs. Kenneth G. Furton, Ph.D. and Stefan Rose, M.D. The research included a study of the abilities of more than a dozen drug canines to detect cocaine. The conclusion of the study, which is summarized in the statement of expert testimony which is attached as Appendix E, is that a positive alert to currency by a trained drug canine is an indication that the currency had recently been in close proximity to controlled substances, and is not the result of alleged innocent environmental contamination of circulated currency by microscopic traces of cocaine. The agency which relies on the canine alert in currency forfeiture cases should be encouraged by the results of this study, and should disseminate it whenever possible.

3 Judicial Treatment of the Canine Alert

[This section surveys the law on dog sniff evidence, from the DEA's perspective, dividing its many case discussions into categories involving airline passengers, vehicles, packages in transit, trains and buses, buildings, and "persons" in general.] [ED. NOTE: Some significant cases are surveyed in *Something May Be Rotten in the State of Drug Detection*, 12 CrimPracReport 444 (11/4/98)], and see BNA CrimPracManual 51:101[4][b][iii], 51:501[5].]

4 Preparing The Canine Handler For Trial

The canine handler, having followed the proper procedures . . . , must still be prepared to persuade a judge or jury that the canine is competent to detect the scent of drugs and that the handler is competent to interpret the canine's message. The government counsel, likewise, should be prepared to counter challenges to the canine's evidence, which often takes the form of evidence of currency contamination.

4.1 Predicate questions for direct examination of canine handler

[Preliminary questions call for handler's credentials, including training with the dog in issue, and the dog's training.]

4. Has the canine been trained on controlled substances or "pseudo-substances"? Is it better to train a canine on controlled substances? What do you use when training your canine?

5. Describe the process by which the canine is certified to detect drugs and you are certified to handle the canine. How often are you each recertified and describe that process?

6. How many hours per week do you train your canine? Describe the training activities and explain the importance of these activities to the canine's performance. Do you document this training?

7. Have you ever discovered that your canine was alerting to a scent other than a drug scent, and, if so, what steps have you taken to correct that behavior? Have you documented these instances?

8. Has the canine ever alerted and a subsequent search failed to reveal either drugs or money? In those instances, has your follow-up discovered evidence to suggest that drugs were in fact present at one time in that area? Have you documented these instances?

9. What quantity of drugs has your dog been trained on and what quantity do you use when training your dog?

10. How many times have you used your canine to examine currency? How many times has it alerted? Do you document those occasions when it has not?

11. Have you ever tested your canine with currency drawn from a bank to determine if your canine is mistakenly alerting just to the scent of currency in general circulation? Have you documented those instances?

12. Some people believe that most of the currency in general circulation is contaminated with drug residue, and that therefore a canine will always alert to currency, even currency in [sic] a bank. Based on your tests with currency drawn from banks, is that a legitimate belief?

13. When seized currency is to be tested by canine, how is the testing area prepared and how is the currency handled to insure that the canine is not alerting to a scent other than the scent of drugs?

4.2 Challenging currency contamination evidence

The challenge to the canine alert which does not focus on the canine itself may take the form of an attack on the substance of the canine's "testimony," particularly where the canine alerts to currency. The most popular attack consists of a witness or publication whose central thrust is that the canine alert is meaningless because the majority of currency in circulation is contaminated with drug residue. . . . The most disturbing aspect of this matter is that courts are accepting this information into evidence and are relying on it to strike down forfeitures. . . .

The weak link in the contamination proponent's argument is the presupposition that a direct correlation exists between the presence of micrograms of drugs on currency and the drug canine's reaction, and therefore, the mere presence of microscopic contamination on a dollar bill will trigger a canine alert. This is the premise that Drs. Furton and Rose effectively refuted in their study of drug canines, a synopsis of which is attached as Appendix E. As Drs. Furton and Rose demonstrate, this presupposition ignores the scent factor—that canines alert to the scent generated by drugs, and that the scent generation is governed by level of contamination and the time the contaminated object is exposed to the air. Their study effectively disproves any correlation between "environmental" contamination of currency and canine alert. In addition to this study, the testimony of the canine handler, with appropriate documentation, that money drawn from banks routinely does not trigger a canine alert, should effectively refute the "currency contamination" theory.

[The guide says that if evidence of currency contamination is proffered, the prosecutor should try to show how the dog's alert in the instant case is "more probative" than others that have "generated criticism." Further, the guide suggests that the best evidence rule, Fed. R. Evid. 1002, may be invoked to bar "all but the original report" of currency tests, and that unless presented by their authors, all reports on test results may be objected to as hearsay. And requests for judicial notice of currency contamination should be opposed as failing to meet the requirement of Fed. R. Evid. 201(b) that a fact be commonly known or readily determinable through unquestionably reliable sources. Citing *U.S. v. Carr*, 25 F.3d 1194, 1202 n.3 (CA3 1994).]

Finally, the report of tests on currency may be attacked as invalid due to an inadequate quantity of tests performed. [Footnote cites Imwinkelried, *The Methods of Attacking Scientific Evidence*, §§ 10-6(A), 13-9 (2d ed. 1992); and Robert Knabe, Esq., *The Contaminated Money Theory: Does It Really Diminish the Significance of a Dog Alert in a Forfeiture Case*, Metro Dade Police Department, Florida. [ED. NOTE: No more information is given in the latter citation. Knabe is identified on the first page of Dr. Furton's curriculum vitae package as a special assistant U.S. attorney, SDFla.] A sampling of the whole, in order to be statistically significant, must be representative of the sample pool. In light of the fact that there is approximately $449,589,400,000 in circulation, an analysis of 100 bills for evidence of contamination still is a sample of only 0.00002224251728355% of the currency in circulation.

DEA MEMORANDUM ON DRUG RESIDUE ON CURRENCY

Excerpt from the DEA Guide's Appendix D, a memorandum on ionscan detection devices dated May 3, 1996, from DEA Deputy Chief Counsel Robert T. Richardson to Michael S. Connolly, Special Agent, Concord Resident Office. As mentioned above, it provides a date for a much-quoted DEA memorandum on drug contamination of currency.

[Initially, the memorandum recognizes that IMS technology has not yet been generally recognized as a means of obtaining probable cause for search and seizure purposes. See *Ezenwa v. Gallen*, 906 F.Supp. 978 (MDPa 1995). It distinguishes the use of the technology in forfeiture cases.]

IMS technology is used to analyze drug residue in the forfeiture context solely to provide additional evidence to support the forfeiture. On currency seizures, containers are analyzed for drug residue in hopes of corroborating the canine alert.

A July 12, 1985, report from the DEA's North Central Lab found drug contamination of a large percentage of the tested currency in general circulation. That finding has been misconstrued by attorneys as supporting the proposition that all currency in general circulation is contaminated. Any discussion of currency contamination presents a hazard of providing support to that proposition, which this office opposes.

As damaging to the use of drug canines to support forfeiture as the results of the 1985 North Central Lab study (as misconstrued by the defense bar) have proven to be, that study did at least analyze all of the residue which could be extracted from a sample of currency by means of a chemical wash. In contrast, the IMS extraction, which employs a "fanning" technique to shake residue from a bundle of currency, does not remove all of the residue from the currency. If the purpose for analyzing drug contamination on currency is to support the position that the currency was recently in close proximity to drugs, there is little benefit of [sic] employing less exact, less complete, subjective methodology.

Federal courts have held that mere evidence of drug contamination of currency does not prove that the currency is drug proceeds. Indeed, the July 12, 1985, report from the DEA's North Central Lab which concluded that drug contamination can be found on currency in general circulation has repeatedly been used to attack the probative value of canine alerts on seized currency. [Footnote cites *U.S. v. $5,000*, 40 F.3d 846 (CA6 1994); *U.S. v. $67,200*, 957 F.2d 289 (CA6 1992); *U.S. v. $30,060*, 39 F.3d 1039 (CA9 1994); *U.S. v. $80,760*, 781 F.Supp. 462 (NDTex 1991).]

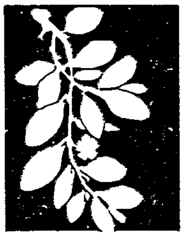
EXHIBIT 11

Volume 7 Issue 1 January 1995 ISSN 1048-8731

Forensic Drug Abuse Advisor

A Monthly Digest of Information on the Forensic Aspects of Drug Abuse

A DEFINITIVE INFORMATION SOURCE FOR MEDICAL, LEGAL, AND SUBSTANCE ABUSE PROFESSIONALS



ALSO IN THIS ISSUE

C M E

The University Medical Center of Southern Nevada designates the Forensic Drug Abuse Advisor as continuing medical education (CME) activity for 15 credit hours in Category 1 of the Physician's Recognition Award of the AMA. Quizzes are sent each February and August.

Money Matters – Currency Contamination and the Law

Until last November, federal courts allowed the use of drug-sniffing dogs to establish probable cause for a search. If a trained dog signaled its handlers that cocaine was present on currency, or anything else for that matter, police could use the dog's reaction as probable cause for a search. But in mid-November, the 9th U.S. Circuit Court of Appeals ruled that this approach was no longer valid. The court held that just because a dog detected cocaine on currency it did not prove anything about the activities of the person holding the currency. The reason behind the decision is that most of the currency in the United States is contaminated with cocaine. Everyone may have contaminated money in their possession, not just criminals.

The ruling was the result of a case in which a 30 year old man was stopped by police in 1990, allegedly for running a stop sign. The arresting officers said they saw a plastic bag filled with money on the seat of the car. A drug-detecting dog was brought to the scene and it signaled the presence of drugs. No drugs were found, however, and the charges were subsequently dropped, but the federal government kept the money anyway, claiming that it had been obtained by drug dealing. The man who had been arrested sued to get his money back and he won. The federal government appealed the decision.

The Circuit Court heard evidence from toxicologists that, in some cities, up to 75% of the money supply is contaminated, and also that cocaine can be transferred from contaminated money onto the hands of innocent people. Based on that knowledge, the Court upheld the findings of the trial judge, arguing that, given the degree of contamination, the possession of contaminated money could not be used to prove criminal behavior.

The observation that the U.S. money supply is contaminated is not exactly new. Several years ago, a toxicologist in the Dade County (Miami) Medical Examiner's office collected $20 bills from prominent Miami citizens, including U.S. Attorney General Janet Reno. All of the

bills tested positive for cocaine. But the wisdom of the Appeals Court decision is born out by two presentations at the SOFT (Society of Forensic Toxicologists) meeting recently held in Tampa, Florida.

Jonathan Oyler, and his colleagues at the Addiction Research Center (ARC), obtained ten one dollar bills from eight different cities around the United States. Individual bills were extracted with methanol and the extract purified by solid phase extraction. The extract was then analyzed using GC/MS. The values obtained were compared against standard curves made by analyzing new, uncirculated dollar bills. Only 70% of the dollar bills from Chicago tested positive, giving the windy city the lowest rate of contamination. Honolulu, on the other hand, had a perfect score with ten out of ten bills testing positive. Baltimore, Kansas City, Las Vegas, Los Angeles, and Mobile scored at 90% positive.

Oyler also calculated the maximum amount of cocaine per dollar bill. Values ranged from a low of 10µg/bill in Honolulu, to 434 µg/bill in Minneapolis and 522 µg/bill in Baltimore. Whether or not anything can be inferred about patterns of abuse based on the amount of cocaine on the money remains to be seen.

Had the court ruled in favor of the federal government, the plaintiff could have used the findings of a second SOFT presentation to get his money back. He could have claimed that, no matter how well dogs are trained, they cannot reliably detect cocaine. Toxicologists from Arkansas tested three Arkansas State Police dogs under controlled conditions. New, uncirculated currency was obtained, then contaminated with cocaine. The dogs were then exposed to contaminated and uncontaminated bills in a series of experiments.

In the first set of experiments, the dogs were exposed to four different samples of the new, uncontaminated, currency. All three dogs responded to three of the four samples as if they contained cocaine. Since it was obvious that the dogs were responding to uncontaminated currency, the researchers used unprinted plain bond paper, some of which had been contaminated with large amounts of cocaine (up to 5000µg/bill). None of the dogs responded to plain bond controls, and they inconsistently responded to bond that had been contaminated.

The authors concluded that their studies proved that "this group of dogs falsely alerted to drug-free currency and paper," and that "considerable variability exists from dog to dog with respect to cocaine detection," and that "no clear dose-response relationship was evident for these dogs under these conditions."

COMMENT: Of course, if the money supply is completely contaminated, and it appears to be, that raises other questions. Do drugs get transferred onto the hands of non-drug users just by handling contaminated currency? And if it does, does enough get onto the hair to cause false positive hair tests? Or, do small amounts get absorbed through the skin, causing low levels of metabolite to appear in urine and hair? If that were the case, then the results would constitute a powerful argument against hair testing. But the experiments that would answer these questions have yet to be done.

Shampoo and Drugs: Hair Washing Tips For Drug Users

Drug users might be well advised to be careful about their choice of hair shampoo. Researchers at the University of Alabama have found that some shampoos will make drug detection more likely, while others may conceal drug use. Cocaine-negative hair was obtained from a Black, an Asian, and a Caucasian. The hair samples were then washed in one of 12 different commercially available shampoos. After washing, each hair sample was soaked for eight hours in a solution containing 1µg/ml of cocaine and 0.1M phosphate buffer (pH 6.0). After soaking, the samples were washed in methanol and phosphate buffer. The cocaine content of each hair sample was then measured using GC/MS.

The final cocaine concentration measured in the hair samples varied depending on which shampoo was used, and the racial origin of the hair. In Caucasian hair concentrations ranged from 3.1 to 8.8 ng/mg. In Asian hair concentrations ranged from 5.3 to 9.6 ng/mg. In Black hair concentrations ranged from 5.5 to 15.5 ng/mg.

EXHIBIT 12

Washington's sniffer dogs re-trained to ignore pot and focus on hard drugs

Police in Washington, where voters legalized marijuana use last year, putting dogs on marijuana desensitization training

Associated Press: Friday 31 May 2013 17.34 ED

When Dusty, a 19-month-old black Labrador, walked past a pipe full of marijuana during a recent police search of a house, he was doing exactly what his handler hoped.

The newest drug-sniffing dog on the police force in Bremerton, near Seattle, is one of a few police dogs in Washington state that are not trained to point out pot during searches. Other police departments are considering or in the midst of re-training their dogs to ignore pot as well, part of the new reality in a state where voters last fall legalized marijuana use.

"We wanted to train our dog on what was truly illegal substances, that would be heroin, methamphetamine and cocaine," said Dusty's handler, Officer Duke Roessel, who added that Dusty nabbed 5lbs of meth during that recent search.

Police departments in Bremerton, Bellevue and Seattle, as well as the Washington state patrol, have either put the dogs through pot desensitization training or plan not to train them for marijuana detection.

The law decriminalized possession of up to an ounce of the drug for individuals over 21 years old. It also barred the distribution and growth of marijuana outside the state-approved system.

Police say that having a K-9 unit that doesn't alert to pot will lessen challenges to obtaining search warrants because the dog won't be pointing out possible legal amounts of the drug. Traditionally, dogs are trained to alert on the smell of marijuana, heroin, crack cocaine, methamphetamine and cocaine. They can't tell which one it is or how much of each there is.

In December, the Washington Association of Prosecuting Attorneys told officers in a guidance memo that dogs that alert on pot face limitations when a search warrant is sought but those are "not fatal to a determination of probable cause."

The group instructed officers to point out that the dog was trained to smell pot and how that is relevant to other information when they seek a warrant, and that a "narcotics-trained canine's alert will still be relevant to the probable cause equation."

In Pierce County, however, prosecutor Mark Lindquist said authorities are being cautious about the new law because judges might excise the dog sniff from their analysis of

probable cause. He's also not convinced dogs can be re-trained. "We'll need new dogs to alert on substances that are illegal," he said.

In January, the Washington State Criminal Justice Training Commission removed detecting marijuana from its canine team certification standards. The change doesn't prohibit trainers from doing so, but it's not required anymore.

But some police departments aren't making any changes. And some observers say that a state Supreme Court decision in 2010 in which the justices sided against medical marijuana patients who argued police officers no longer had probable cause to immediately arrest or investigate due to the legalization of medical pot.

Last fall's legalization law "just made one ounce not a crime for adults. That means that any amount over an ounce is still illegal, growing marijuana is still illegal, selling marijuana is still illegal, passing a joint to somebody is still illegal," said medical marijuana advocate and attorney Douglas Hiatt.

For different reasons, dog trainer Fred Helfers of the Pacific Northwest Detection Dog Association agreed with Hiatt.

But having spent 20 years as a narcotics investigator, Helfers said departments who abandoned pot training are having a "knee-jerk" reaction. He said they may miss actual crimes being committed. "What about trafficking? What about people who have more than an ounce?" he said.

Nonetheless, Helfers is helping departments who want to go through the "extinction" training, which he said is a common method to change what substances dogs alert to. It takes about an initial 30 days plus every day reinforcements to modify the dog's behavior.

"Overall, I think there's still a large amount of agencies on a wait-and-see approach with their dogs," Helfers said.

http://www.theguardian.com/world/2013/may/31/washington-sniffer-dogs-marijuana